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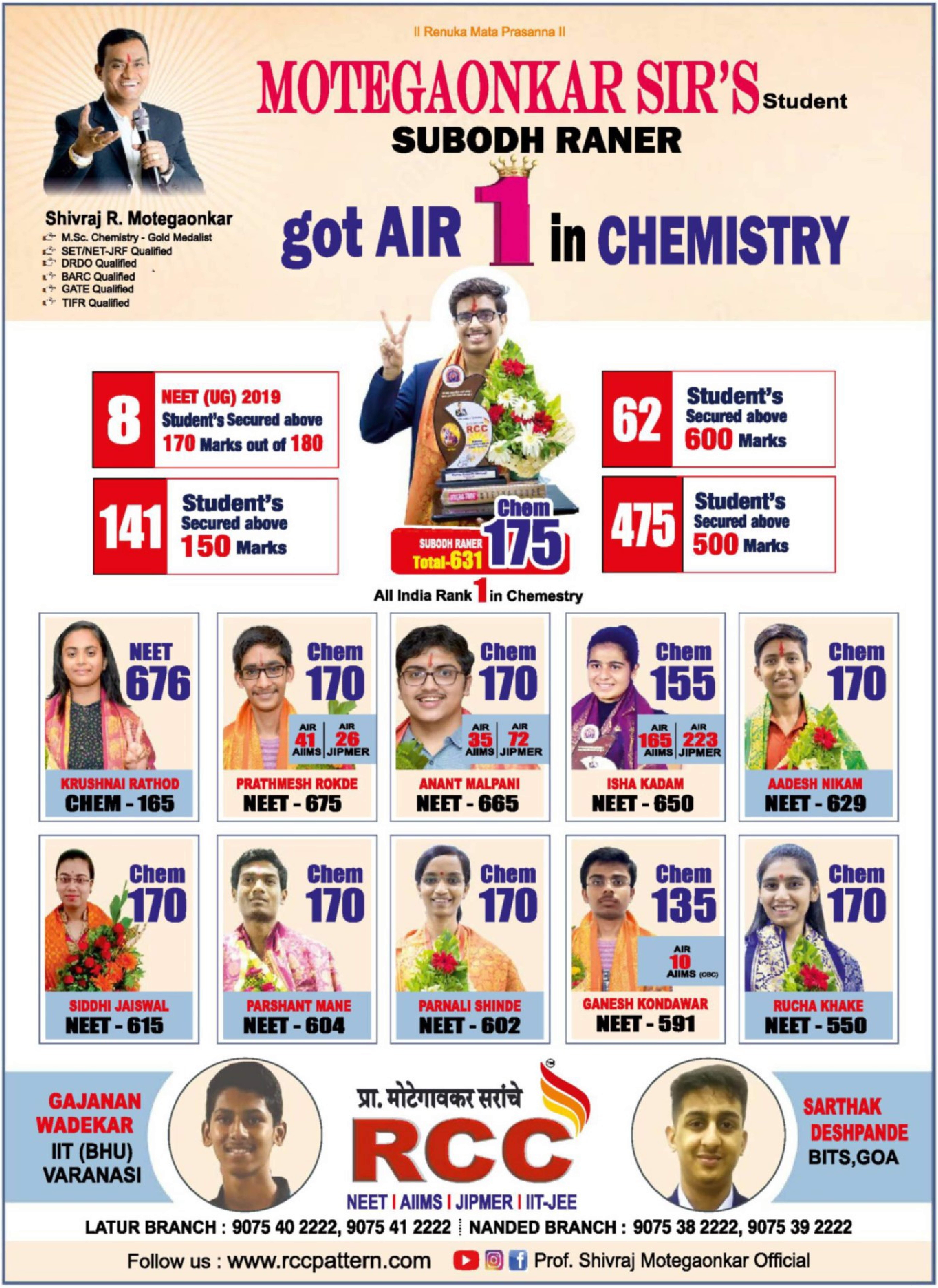

II Renuka Mata Prasanna II
MOTEGAONKAR SIR'S Student
SUBODH RANER
got AIR 1 in CHEMISTRY
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M.Sc. Chemistry - Gold Medalist
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8 NEET (UG) 2019 Student's Secured above 170 Marks out of 180
141 Student's Secured above 150 Marks
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All India Rank 1 in Chemestry
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Chem 170 AIR 41 AIIMS AIR 26 JIPMER PRATHMESH ROKDE NEET - 675
Chem 170 AIR 35 AIIMS AIR 72 JIPMER ANANT MALPANI NEET - 665
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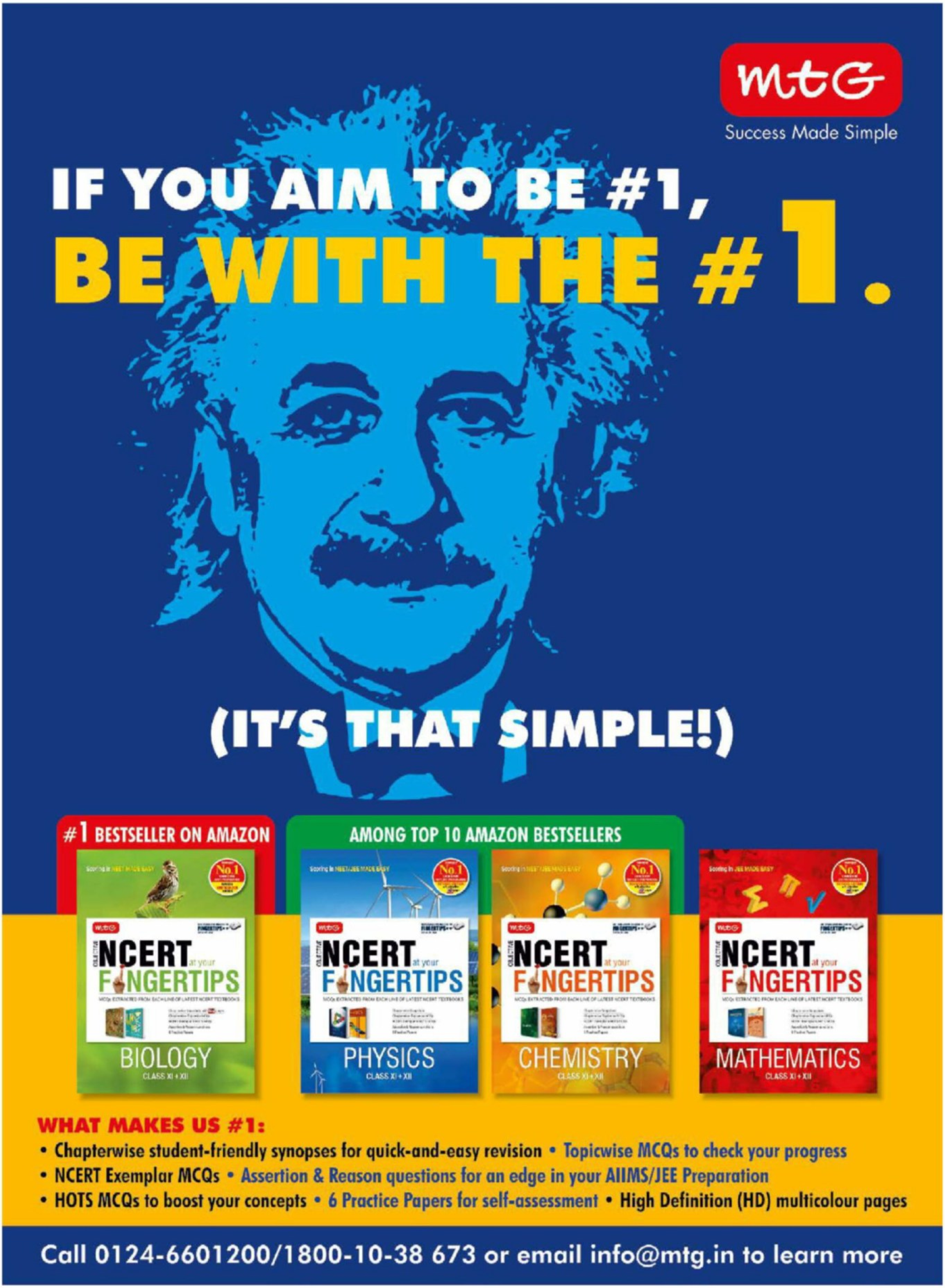
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Managing Editor
Mahabir Singh

Editor
Anil Ahlawat

Corporate Office:
Plot 99, Sector 44 Institutional area, Gurugram -122 003 (HR).
Tel : 0124-6601200 e-mail : info@mtg.in website : www.mtg.in

Regd. Office:
406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

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Editor : Anil Ahlawat

GET SET GO *for* NEET

Exam on May 3, 2020

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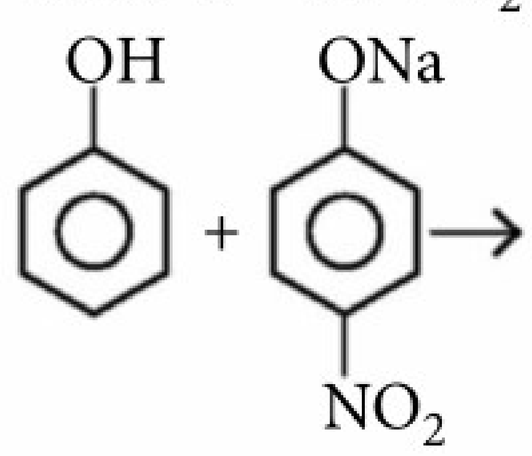
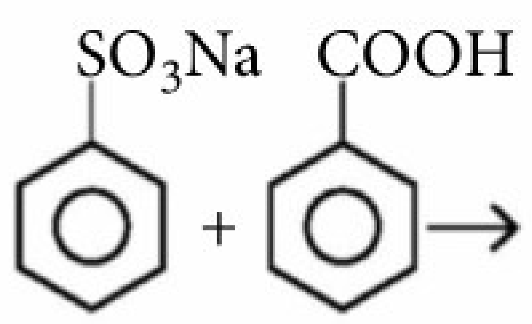
1. Which of the following gives propyne on hydrolysis?
(a) Al_4C_3 (b) Mg_2C_3 (c) B_4C (d) La_4C_3

2. The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement about the nature of HCl is
(a) 17% ionic (b) 83% ionic
(c) 50% ionic (d) 100% ionic.

3. For the four gases *A*, *B*, *C* and *D*, the value of the excluded volume per mole is same. If the order of the critical temperature is $T_B > T_D > T_A > T_C$, then the order of their liquefaction pressure at a temperature *T* will be
(a) $P_A < P_B < P_C < P_D$ (b) $P_B < P_D < P_A < P_C$
(c) $P_C < P_A < P_D < P_B$ (d) $P_D < P_C < P_A < P_B$

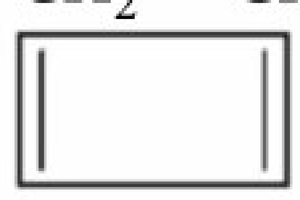
4. Which of the following reactions is feasible?
(a) $CH_3COOH + HCOONa \longrightarrow$
(b) $HC \equiv C - Na + H_2O \longrightarrow$
(c) 
(d) 

5. The wave number of the first line in the Balmer series of hydrogen is 15200 cm^{-1}. What would be the wave number of the first line in the Lyman series of the Be^{3+} ion?
(a) $2.4 \times 10^5\ cm^{-1}$ (b) $2.0 \times 10^5\ cm^{-1}$
(c) $6.08 \times 10^5\ cm^{-1}$ (d) $1.313 \times 10^6\ cm^{-1}$

6. The reaction, $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$, is spontaneous. The $\Delta S° = -163.1\ J\ mol^{-1}\ K^{-1}$. The absolute entropies of $H_{2(g)}$ and $O_{2(g)}$ are 130.6 $JK^{-1}\ mol^{-1}$ and 205 $JK^{-1}\ mol^{-1}$ respectively. What will be the absolute entropy ($JK^{-1}\ mol^{-1}$) of water?
(a) 73.2 (b) 65.6 (c) 70.0 (d) 75.5

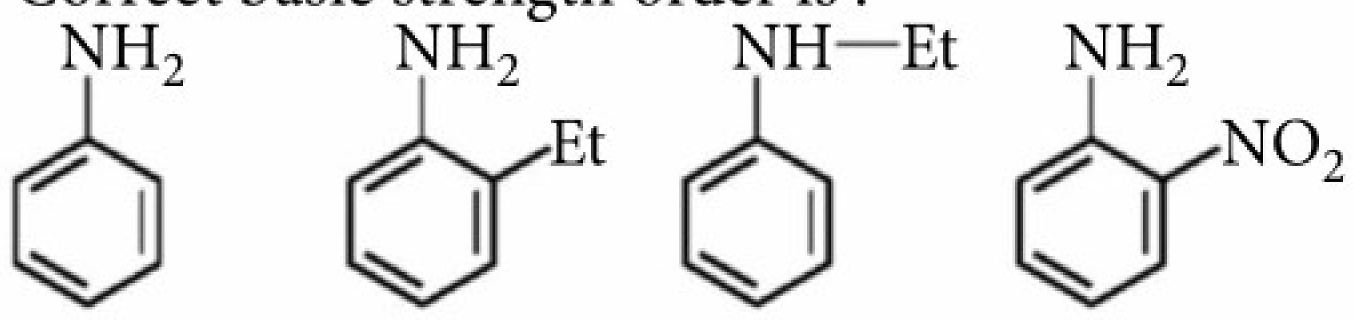
7. The predominating product for the following reaction is

$$\underset{\substack{|\\Br}}{CH_2}-CH=CH-\underset{\substack{|\\Br}}{CH_2} \xrightarrow{Zn,\ CH_3OH} \text{Product}$$

(a) 
(b) $CH_2=C=C=CH_2$
(c) $CH_2=CH-CH=CH_2$
(d) 

8. What is the atomic number of Livermorium ?
(a) 106 (b) 96 (c) 116 (d) 118

9. Correct basic strength order is :



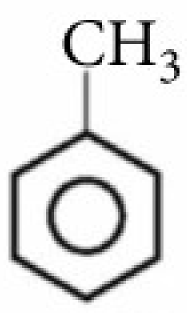
P Q R S

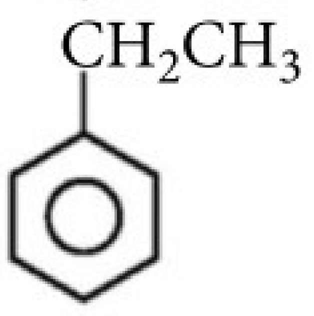
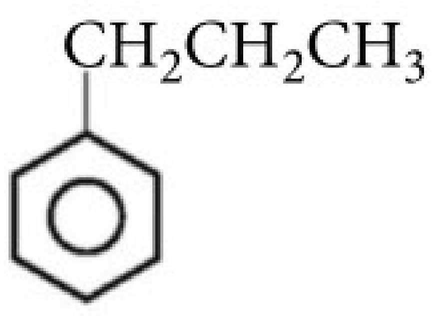
(a) $R > Q > P > S$ (b) $R > P > Q > S$
(c) $Q > R > P > S$ (d) $R > Q > S > P$

10. When gypsum is totally dehydrated, what is the percentage weight loss?
(a) 20.9 (b) 17.6 (c) 19.0 (d) 21.5

11. In the following reaction, the product R is

$$CaC_2 \xrightarrow{H_2O} P \xrightarrow[873\text{ K}]{\text{Red hot iron tube}} Q \xrightarrow[\text{anhy. }AlCl_3]{CH_3Cl} R$$

(a)  (b) 

(c)  (d) 

12. Dissociation constant of a weak acid HA is 10^{-7}. 10 mL of aqueous HA of pH value 4 is added with 990 mL of water. Calculate the final pH of acid HA.
(a) 5 (b) 6 (c) 7 (d) 8

13. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is
(a) 6 (b) 3 (c) 1/6 (d) 1/3

14. An oxide of carbon (X) reacts with ammonia to produce urea, an important fertilizer. Which of the following combinations will not yield (X)?
(a) $CO_3^{2-} + HCl \xrightarrow{\Delta}$ (b) $CaO + C \xrightarrow{\Delta}$
(c) $C + O_{2(excess)} \xrightarrow{\Delta}$ (d) $HCO_3^- + HCl \xrightarrow{\Delta}$

15. A synthetic mixture of nitrogen and argon has a density of 1.4 gL^{-1} at 0 °C and 1 atm pressure. Its average molecular weight and volume percentage of nitrogen in the mixture will be
(a) 25.6 and 50 (b) 31.4 and 72
(c) 70 and 31.4 (d) 50 and 25.6

SOLUTIONS

1. **(b) :** $Mg_2C_3 + 4H_2O \rightarrow CH_3C\equiv CH + 2Mg(OH)_2$

2. **(a) :** % ionic character $= 16(X_A - X_B) + 3.5(X_A - X_B)^2$
$= 16(3 - 2.1) + 3.5(3 - 2.1)^2 = 16 \times 0.9 + 3.5\,(0.9)^2$
$= 14.4 + 2.836 = 17.236 = 17\%$

3. **(b)** 4. **(b)**

5. **(d) :** Given $15200 = R(1)^2\left[\frac{1}{(2)^2} - \frac{1}{(3)^2}\right]$ ...(i)

Then $\bar{\nu} = R(4)^2\left[\frac{1}{(1)^2} - \frac{1}{(2)^2}\right]$ ...(ii)

From equation (i) and (ii)
$\bar{\nu} = 1.313 \times 10^6 \text{ cm}^{-1}$

6. **(c) :** Change in standard entropy,

$$\Delta S^\circ = S^\circ_{H_2O(l)} - \left[S^\circ_{H_2} + \frac{1}{2}S^\circ_{O_2}\right]$$

$$-163.1 \text{ J mol}^{-1}\text{ K}^{-1} = S^\circ_{H_2O(l)} - \left[130.6 + \frac{205}{2}\right]$$

Absolute entropy of water = 70.0 JK^{-1} mol^{-1}.

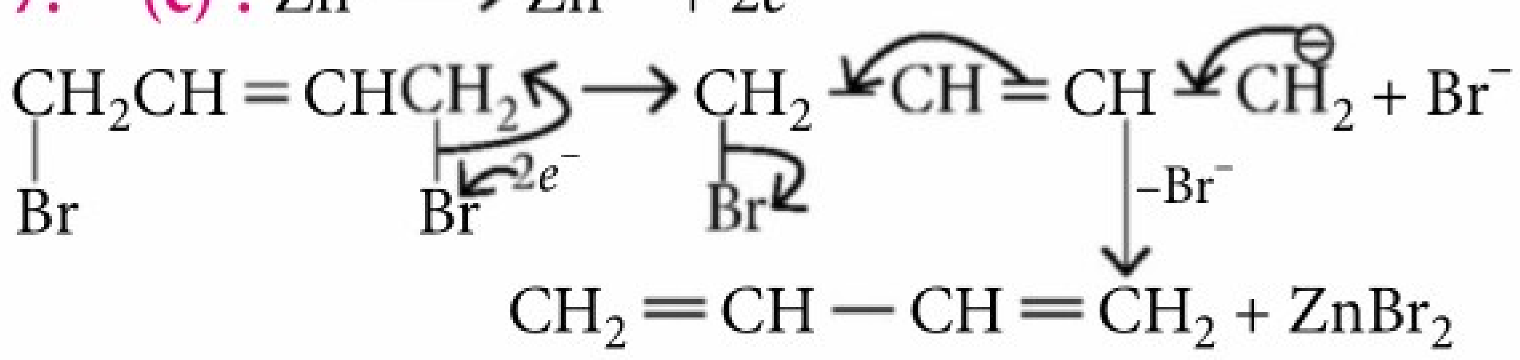
CHEMISTRY PUZZLE

OCTOBER 2019

Try to find as many as words related organic chemistry. Readers can send their responses at editor@mtg.in or post us with complete address by 10th of every month. The name of the reader who will give more than twenty correct answer, will be published in next issue.

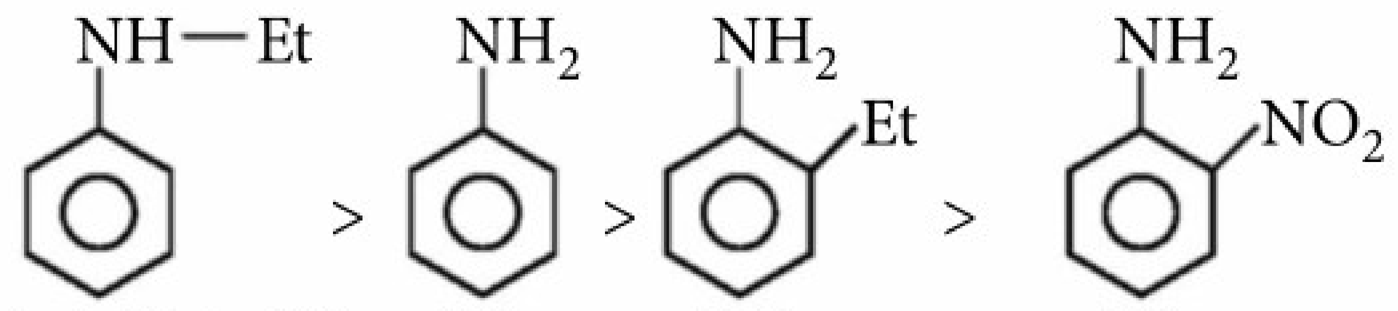
I	A	D	C	E	S	T	E	R	I	F	I	C	A	T	I	O	N	S	T	A	I
A	C	X	R	T	M	S	W	O	A	K	Q	Z	O	N	A	J	E	C	V	D	W
S	H	Y	P	E	R	C	O	N	J	U	G	A	T	I	O	N	I	K	L	N	A
N	R	Q	S	T	N	K	S	E	I	M	N	S	T	W	A	C	M	P	R	Q	S
X	I	P	E	A	D	A	C	O	N	D	E	N	S	A	T	I	O	N	C	R	P
A	W	S	X	C	Q	A	C	I	J	L	M	N	S	T	E	O	N	R	O	T	U
C	L	N	I	Q	A	L	K	A	N	E	X	U	I	T	T	N	O	M	M	S	N
I	K	D	A	N	B	R	E	S	O	N	A	N	C	E	H	M	H	C	B	F	S
D	I	Q	E	A	G	I	B	E	N	Z	E	N	E	G	E	H	Y	J	U	K	A
A	F	E	P	H	D	L	C	O	B	R	S	A	Q	O	R	D	D	G	S	L	T
N	S	N	O	R	Y	I	E	J	X	B	I	N	D	T	V	R	R	I	T	P	U
H	S	P	Q	L	K	D	J	B	I	Y	X	H	W	V	N	T	O	S	I	Q	R
Y	T	N	S	I	V	Q	E	M	O	R	L	A	D	E	X	Y	X	Q	O	P	A
D	X	Z	A	C	E	R	S	D	Q	N	N	I	P	O	L	N	Y	I	N	S	T
R	C	E	R	Q	N	I	E	A	M	I	D	E	C	C	B	E	F	I	H	G	E
I	H	N	P	Q	R	T	S	U	X	E	N	D	A	A	L	K	E	N	E	R	D
D	O	W	R	E	A	P	T	A	B	F	G	I	H	D	C	A	C	T	P	Q	R
E	P	R	M	R	S	K	E	T	O	N	E	X	Y	A	R	I	E	A	Z	O	C
A	D	O	U	T	X	A	R	O	M	A	T	I	C	N	O	P	D	L	Y	N	D
C	S	T	W	Q	P	S	T	N	O	B	S	R	Q	T	Y	N	X	K	O	P	A
I	A	N	F	O	X	I	D	A	T	I	O	N	Q	D	A	O	Z	Y	A	Z	C
S	A	P	O	N	I	F	I	C	A	T	I	O	N	P	C	Y	O	L	C	P	A

7. (c) : $Zn \longrightarrow Zn^{2+} + 2e^-$



8. (c)

9. (b) :



(+ *I* effect of Et) (*R*) > (*P*) > (*Q*) > (*S*)

(*Q*): *ortho*-effect of Et is base weakening effect.

(*S*): –*I* and *ortho*-effect of NO_2 are base weakening effects.

10. (a) : Molecular weight of gypsum, $CaSO_4 \cdot 2H_2O = 172$ g

Weight of water of hydration = 2 × 18 = 36 g

172 g loses 36 g of water on dehydration.

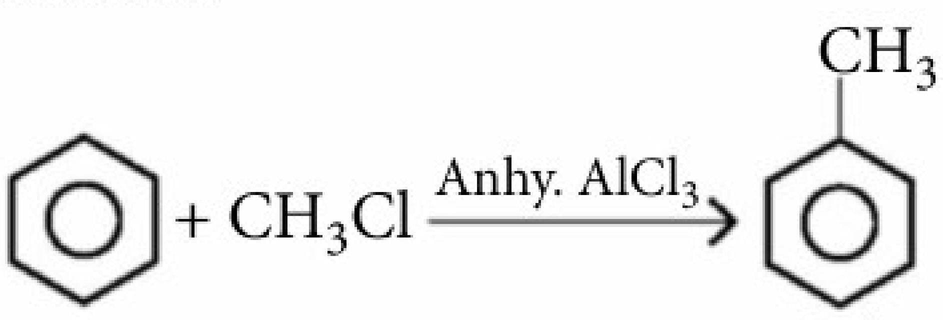
Percentage weight loss $= 36 \times \frac{100}{172} = 20.9$

11. (b) : Hydrolysis of calcium carbide produces acetylene with calcium hydroxide.

$$CaC_2 \xrightarrow{2H_2O} \underset{(P)}{C_2H_2} + Ca(OH)_2$$

$3C_2H_2$ (*P*) $\xrightarrow[873\text{ K}]{\text{Red hot iron tube}}$ (*Q*) Benzene

This is the synthetic method for the preparation of benzene.



+ CH_3Cl $\xrightarrow{\text{Anhy. } AlCl_3}$ (*R*) Toluene

This is known as Friedel-Craft's alkylation reaction, which results in production of homologue of arene.

12. (a) : Given, pH = 4, $[H^+] = 10^{-4}$ M

$[H^+] = \sqrt{K_aC}$, $10^{-4} = \sqrt{10^{-7}C}$

Initial concentration of the weak acid, $HA = C = 0.1$ mol L^{-1}

Final concentration of the acid $HA = \frac{10 \times 0.1}{1000}$

$= 10^{-3}$ mol L^{-1}

$[H^+] = \sqrt{K_aC} = \sqrt{10^{-7} \times 10^{-3}} = 10^{-5}$ M

pH = –log 10^{-5} = 5 log 10 = 5

13. (d) :

$$\begin{array}{rl} Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow & 2Cr^{3+} + 7H_2O \\ Sn^{2+} \longrightarrow & Sn^{4+} + 2e^-] \times 3 \\ \hline Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow & 2Cr^{3+} + 3Sn^{4+} + 7H_2O \end{array}$$

Here 3 moles of Sn^{2+} ions reduce $K_2Cr_2O_7$ = 1 mole

∴ 1 mole of Sn^{2+} ions will reduce $K_2Cr_2O_7$ = 1/3 mole.

14. (b) : (*X*) is CO_2 because CO_2 and NH_3 under pressure gives urea which is used as a fertilizer. Reaction (b) does not produce CO_2

$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$

15. (b) : Molecular weight (*M*) can be obtained from density (*d*) as, $M = \frac{dRT}{P}$

Average molecular weight of the mixture

$= \frac{1.4 \times 0.0821 \times 273}{1} = 31.4$

If the % volume of N_2 is '*x*'.

$31.4 = \frac{x \times 28 + (100 - x)40}{100}$

$\Rightarrow 12x = 860 \quad \Rightarrow \quad x = 71.6 \simeq 72$

Thus, volume percentage of N_2 in the mixture = 72

◆◆

EXAM ALERT — NEET 2020 DATE SHEET RELEASED

The entrance exam for the MBBS/BDS courses in India — National Eligibility cum Entrance Test (NEET) for undergraduate courses is going to be held on **May 3, 2020 (Sunday)**. This is the second time the National Testing Agency (NTA) will be conducting the NEET. The application process will begin from December 2 and will close on December 31. Interested candidates can apply at **ntaneet.nic.in**.

All those candidates who have passed class 12 are eligible to appear for the National Eligibility Entrance Test (NEET UG 2020). The exam will be held in the pen-and-paper mode and from **March 27,** the applicants can download the **NEET admit card**. The result for NEET is scheduled to release on **June 4**.

NEET is a three-hour long exam which includes three sections – physics, chemistry and biology. Of the total 180 questions, 90 would be from biology and 45 each from physics and chemistry. Preparation syllabus includes the whole of class 11 and 12 standard NCERT textbooks in the respective subjects.

Every correct answer would get plus four marks and every incorrect answer result in a negative mark. Questions that are not attempted do not have any penalty marks. The National Testing Agency (NTA) has been set-up by the government of India responsibility of NTA to conduct the entrance test. Competitive entrance exams including NEET UG, JEE, NET, etc. were earlier conducted by CBSE. In NEET 2019, record 15 lakh candidates applied and the exam was held on May 5.

CLASS-XI

BRUSH UP for NEET/JEE 2020

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 4 Equilibrium | Redox Reactions

Equilibrium

- Equilibrium is the state of reaction which proceeds in both the forward and backward directions at the equal speed or the state of chemical reaction in which concentrations of reactants and products become constant at constant temperature and pressure irrespective of the initial state.
  Equilibrium is of two types :
  (i) Physical equilibrium (ii) Chemical equilibrium

Physical Equilibrium

It is the process which involves only, physical changes like equilibrium between different states of substances at a particular temperature.

- Solid $\rightleftharpoons$ Liquid : ice $\rightleftharpoons$ water at 0 °C
  rate of melting = rate of freezing
- Liquid $\rightleftharpoons$ Gas (vapour) :
  water (liquid) $\rightleftharpoons$ water (vapours) at 100 °C
  rate of evaporation = rate of condensation
- Solid $\rightleftharpoons$ Gas (vapour) :
  CO_2 (solid) $\rightleftharpoons$ CO_2 (vapours)
  rate of sublimation = rate of deposition
- Solid $\rightleftharpoons$ Saturated solution of solid in liquid :
  rate of dissolution = rate of precipitation
  sugar (solid) $\rightleftharpoons$ sugar (in solution)
- Gas $\rightleftharpoons$ Saturated solution of gas in liquid; it is always exothermic and spontaneous.
  CO_2 (gas) $\rightleftharpoons$ CO_2 (in solution)

Chemical Equilibrium

If the process involves only chemical changes, the equilibrium is called chemical equilibrium.

- **Reversible reaction :** A reaction in which not only the reactants react to form products but also the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. These reactions if carried out in a closed vessel do not go to completion.
  e.g., $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- **Irreversible reaction :** These are the reactions in which products do not react back to give the reactants, *i.e.*, reaction cannot be retraced at any point. *e.g.*, rusting of iron, etc.
- **State of equilibrium :** Chemical equilibrium is that state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.
- **Dynamic nature of equilibrium :** In dynamic equilibrium, changes occur but in opposite directions and at constant rate *i.e.*, forward and backward reactions take place even after the equilibrium is attained but at equal speeds.

Types of Chemical Equilibrium

- **Homogeneous equilibrium :** In this type of equilibrium reaction, all the reactants and products are present in same phase.
  e.g., $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
  $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
- **Heterogeneous equilibrium :** In this type of equilibrium reaction, reactants and products are present in two or more than two different phases.
  e.g., $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$;
  $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

Law of Chemical Equilibrium and Equilibrium Constant

- For a reversible reaction, $aA + bB \rightleftharpoons cC + dD$
  Rate of forward reaction $(R_f) \propto [A]^a [B]^b = k_f [A]^a [B]^b$
  Rate of backward reaction, $(R_b) = k_b [C]^c [D]^d$
  At equilibrium, $R_f = R_b$
  $\frac{k_f}{k_b} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$; where, K_c is equilibrium constant.
  K_c is specific for a reaction and this equilibrium equation is also known as law of mass action.
- **Relation between equilibrium constants for a general reaction and its multiples :**

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c)^n$
$\frac{1}{n}aA + \frac{1}{n}bB \rightleftharpoons \frac{1}{n}cC + \frac{1}{n}dD$	$K_c''' = \sqrt[n]{K_c}$

- **Relation between K_p and K_c :**
  $$K_c = K_p\left(\frac{1}{RT}\right)^{\Delta n_g} \quad \text{or} \quad K_p = K_c\,(RT)^{\Delta n_g}$$
  If $\Delta n_g = 0$, $K_p = K_c$; If $\Delta n_g = +\text{ve}$, $K_p > K_c$
  If $\Delta n_g = -\text{ve}$, $K_p < K_c$

Units of Equilibrium Constant

- If $\Delta n = 0$, both K_c and K_p have no units.
- If $\Delta n > 0$, unit of $K_c = (\text{mol L}^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm})^{\Delta n_g}$
- If $\Delta n < 0$, unit of $K_c = (\text{L mol}^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm}^{-1})^{\Delta n_g}$

Applications of Equilibrium Constant

- **Predicting the extent of a reaction :** The magnitude of equilibrium constant K indicates the extent to which a reaction can go. In other words, it is a measure of the completion of a reversible reaction. Larger the value of K, greater will be the equilibrium concentration of the components on the right hand side of reaction relative to those on the left hand side, *i.e.*, the reaction proceeds to a greater extent.
- **Predicting the direction of a reaction :** The equilibrium constant helps in predicting the direction in which a reaction can proceed at any stage. By substituting the concentration of substances that exist in a reaction mixture we can calculate the reaction quotient, Q and comparing the value of Q with the equilibrium constant, K, we can predict whether the reaction will proceed towards products or towards reactants.
  Case I : If $Q < K$, the reaction will proceed in the forward direction.
  Case II : If $Q > K$, the reaction will proceed in the backward direction.
  Case III : If $Q = K$, the reaction mixture is already in equilibrium.

Relationship between Gibbs Energy and Equilibrium Constant

- At equilibrium, $\Delta G° = -RT\ln K$; $K = e^{-\Delta G°/RT}$
- If $\Delta G° < 0$ then $K > 1$ [Forward reaction is favoured.]
- If $\Delta G° > 0$ then $K < 1$ [Reversed reaction is favoured.]
- If $\Delta G° = 0$, then $K = 1$ [Reaction is in equilibrium.]

Factors Affecting Equilibria

Le Chatelier's principle : If a system in equilibrium is subjected to change in concentration, pressure or temperature, equilibrium shifts in the direction that tends to undo the change imposed.

- **Effect of change in concentration :** Increase in concentration of reactants favours forward reaction and increase in concentration of products favours backward reaction.
- **Effect of change in temperature :** High temperature favours endothermic reactions and low temperature favours exothermic reactions.
- **Effect of change in pressure :** High pressure favours the direction in which lesser number of moles of the gas are produced and low pressure favours the

direction in which larger number of moles of the gas are produced.

- **Effect of inert gas addition :** Addition of inert gas at constant volume does not affect the equilibrium and addition of inert gas at constant pressure favours the direction in which larger number of moles of the gas are produced.
- **Effect of adding catalyst :** The addition of catalyst does not affect the equilibrium.

PEEP INTO PREVIOUS YEARS

1. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327 °C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327 °C is (R = 0.082 L atm mol^{-1} K^{-1}, Molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1})
   (a) 0.242×10^{-4} atm^2 (b) 0.242 atm^2
   (c) 1×10^{-4} atm^2 (d) 4.9×10^{-3} atm^2
   (JEE Main 2019)

2. Which one of the following conditions will favour maximum formation of the product in the reaction $A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}$, $\Delta_r H = -X$ kJ ?
   (a) Low temperature and high pressure
   (b) Low temperature and low pressure
   (c) High temperature and high pressure
   (d) High temperature and low pressure
   (NEET 2018)

3. The equilibrium constants of the following are
   $N_2 + 3H_2 \rightleftharpoons 2NH_3;\ K_1$
   $N_2 + O_2 \rightleftharpoons 2NO;\ K_2$
   $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;\ K_3$
   The equilibrium constant (K) of the reaction :
   $2NH_3 + \frac{5}{2}O_2 \xrightleftharpoons{K} 2NO + 3H_2O$ will be
   (a) $K_2K_3^3/K_1$ (b) K_2K_3/K_1
   (c) $K_2^3K_3/K_1$ (d) $K_1K_3^3/K_2$
   (NEET 2017, 2007, 2003)

IONIC EQUILIBRIUM

Ionic equilibrium is the equilibrium existing in solution involving ions or reversible reaction that proceeds through ion formation in water. Ionic compound on dissolution in water splits up into ions, this is called ionisation or dissociation. As aqueous solution of ionic compounds have ions of opposite charges, so they are able to conduct electricity.

Ostwald's Dilution Law

- Consider the given reaction,

	AB	$\rightleftharpoons$	A^+	$+ B^-$
Initial concentration	C		0	0
Conc. at equilibrium	$C(1-\alpha)$		$C\alpha$	$C\alpha$

where, α is degree of dissociation.

$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$; where, K_a is called dissociation or ionisation constant.

For a weak electrolyte, $\alpha \lll 1$ and $1 - \alpha \approx 1$

$K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$ or $\alpha = \sqrt{K_aV}$

where, V is the volume, containing one mole of electrolyte.

Concepts of Acids and Bases

- **Arrhenius concept :**
  – Arrhenius acid furnishes hydrogen ions in aqueous solution, *e.g.*, HCl.
  – Arrhenius base furnishes hydroxyl ions in aqueous solution, *e.g.*, NaOH.
- **Brönsted—Lowry concept :**
  – Brönsted acid donates a proton, *e.g.*, HCl.
  – Brönsted base accepts a proton, *e.g.*, NH_3.
- **Conjugate acid - base pairs :** These are a pairs of acids and bases which differ by a proton, *e.g.*,
  Conjugate acid $\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$ Conjugate base
- Relative strengths of conjugate acids or bases depend upon their tendency to donate a proton or to accept a proton.
- Stronger the acid, weaker is its conjugate base and *vice-versa*, for example,
  $\underset{\text{Strong acid}}{HCl_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Weak base}}{Cl^-_{(aq)}}$
  $\underset{\text{Weak acid}}{CH_3COOH_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Strong base}}{CH_3COO^-_{(aq)}}$
- **Lewis concept :**
  – Lewis acid accepts a pair of electrons, *e.g.*, BF_3.
  – Lewis base donates a pair of electrons, *e.g.*, NH_3.
- **Relative strength of acids and bases :** This is the ratio of strengths of two weak acids. *e.g.*, for acids HA_1 and HA_2:
  $HA_1 \rightleftharpoons H^+ + A_1^-;\ K_{a_1} = C_1\alpha_1^2$
  $HA_2 \rightleftharpoons H^+ + A_2^-;\ K_{a_2} = C_2\alpha_2^2$
  Relative strength $= \frac{[H^+] \text{ furnished by } HA_1}{[H^+] \text{ furnished by } HA_2} = \frac{C_1\alpha_1}{C_2\alpha_2}$
  $= \frac{C_1\sqrt{K_{a_1}/C_1}}{C_2\sqrt{K_{a_2}/C_2}} = \sqrt{(K_{a_1}C_1)/(K_{a_2}C_2)}$ $(\because \alpha = \sqrt{K_a/C})$

If concentrations of acids are same ($C_1 = C_2$) then,

Relative strength $= \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

- Similarly, the relative strength of two weak bases of equimolar concentration :

  Relative strength of bases $= \sqrt{\dfrac{K_{b_1}}{K_{b_2}}}$

Ionisation of Acid and Bases

- $\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + A^-, K_a = \dfrac{[H^+][A^-]}{[HA]}$

  and degree of ionisation, $\alpha = \sqrt{\dfrac{K_a}{C}}$

- $\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-, K_b = \dfrac{[B^+][OH^-]}{[BOH]}$

  and degree of ionisation, $\alpha = \sqrt{\dfrac{K_b}{C}}$

Hydrogen Ion Concentration and Ionic Product of Water

$$pH = -\log[H^+] = \log\frac{1}{[H^+]} \text{ or } [H^+] = 10^{-pH}$$

$$pOH = -\log[OH^-] = \log\frac{1}{[OH^-]} \text{ or } [OH^-] = 10^{-pOH}$$

$K_w = [H^+][OH^-]$

$= \text{Ionic product of water} = 10^{-14}\ (\text{mol/L})^2$

$pK_w = -\log K_w;\ pK_w = pH + pOH = 14$

- **Relationship between K_a and K_b or pK_a and pK_b :**

  $pK_a = -\log K_a$; $pK_b = -\log K_b$

  $K_a \times K_b = [H^+][OH^-]$

  So, $K_a \times K_b = K_w$

  or $pK_w = pK_a + pK_b = 14$ (at 298 K)

Hydrolysis of Salts

- It is defined as the process in which a salt reacts with water given back the acid and the base.

  $\underset{\text{Salt}}{B^+A^-} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{Acid}}{HA} + \underset{\text{Base}}{BOH}$

S. No.	Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
1.	Weak acid and Strong base	Anionic	Alkaline	$K_h = \dfrac{K_w}{K_a}$	$h = \sqrt{\dfrac{K_h}{C}}$	$pH = \dfrac{1}{2}[pK_w + pK_a + \log C]$
2.	Strong acid and Weak base	Cationic	Acidic	$K_h = \dfrac{K_w}{K_b}$	$h = \sqrt{\dfrac{K_h}{C}}$	$pH = \dfrac{1}{2}[pK_w - pK_b - \log C]$
3.	Weak acid and Weak base	Anionic and Cationic both	Neutral (almost)	$K_h = \dfrac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = \dfrac{1}{2}[pK_w + pK_a - pK_b]$

Buffer Solutions

- Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.
- **Types of buffer solutions :**

Types	pH
Acidic buffers (pH < 7) (Mixture of weak acid + its salt with a strong base) *e.g.*, $CH_3COOH + CH_3COONa$	(Henderson-Hasselbalch equation) $pH = pK_a + \log\dfrac{[Salt]}{[Acid]}$ or $pH = pK_a + \log\dfrac{[Conjugate\ base]}{[Acid]}$
Basic buffers (pH > 7) (Mixture of weak base and its salt with strong acid) *e.g.*, $NH_4OH + NH_4Cl$	$pH = pK_w - \left(pK_b + \log\dfrac{[Salt]}{[Base]}\right)$ or $pH = pK_a + \log\dfrac{[Base]}{[Salt]}$ or $pOH = pK_b + \log\dfrac{[Salt]}{[Base]}$

Solubility Product

- Solubility product of an electrolyte at a specified temperature may be defined as the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ion produced on dissociation of one molecule of electrolyte.

Salt type	Relation between K_{sp} and S	Examples
AB	$K_{sp} = (S)(S) = S^2$	$AlPO_4$, $AgCl$, $AgBr$, $PbSO_4$, $BaSO_4$, ZnS
AB_2	$K_{sp} = (S)(2S)^2 = 4S^3$	$PbCl_2$, $HgCl_2$
A_2B	$K_{sp} = (2S)^2(S) = 4S^3$	Ag_2CrO_4, $Ag_2C_2O_4$, Ag_2SO_4
AB_3	$K_{sp} = (S)(3S)^3 = 27S^4$	$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$
A_3B_2	$K_{sp} = (3S)^3(2S)^2 = 108S^5$	$Ca_3(PO_4)_2$, $Zn_3(PO_4)_2$

PEEP INTO PREVIOUS YEARS

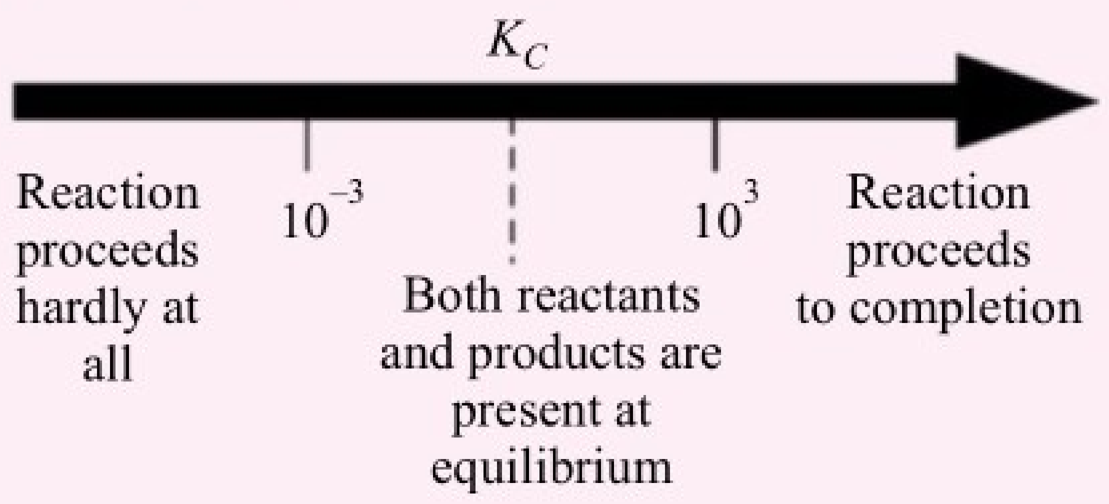
4. Consider the following statements,
(i) The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.
(ii) Ionic product of water is temperature dependent.
(iii) A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
(iv) The Le Chatelier's principle is not applicable to common-ion effect.
The correct statements are
(a) (i) and (ii)
(b) (ii) and (iii)
(c) (i), (ii) and (iv)
(d) (i), (ii) and (iii) ***(JEE Main 2019)***

5. Which will make basic buffer?
(a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(c) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH ***(NEET 2019)***

6. The solubility of $BaSO_4$ in water is 2.42×10^{-3} g L^{-1} at 298 K. The value of its solubility product (K_{sp}) will be (Given molar mass of $BaSO_4$ = 233 g mol^{-1})
(a) 1.08×10^{-10} mol^2 L^{-2}
(b) 1.08×10^{-12} mol^2 L^{-2}
(c) 1.08×10^{-14} mol^2 L^{-2}
(d) 1.08×10^{-8} mol^2 L^{-2} ***(NEET 2018)***

POINTS FOR EXTRA SCORING

- Extent of a reaction :



- Larger the value of K_{sp}, greater is the solubility of salt in water.
- If $K_{ip} > K_{sp}$, precipitation occurs.
- Hard acids are those in which acceptor atoms have small size, high electronegativity, low polarisability and possess noble gas configuration.
- Soft acids are those in which acceptor atoms have large size, low electronegativity, high polarisability and do not have noble gas configuration.
- Hard bases have donor atoms with low polarisabilities and high electronegativity.
- Soft bases have donor atoms with high polarisabilities and low electronegativity.
- Greater the value of ionisation constant of the acid or base, smaller is the pK_a or pK_b and stronger is the acid or base.
- A decrease in pH by one unit indicates 10 times increase in hydronium ion concentration.
- Indicators are organic substances and are generally weak acids or weak bases.
- An acid-base indicator is an organic dye that detect the end point by a visual change in colour.
- Most indicators do not change colour at a particular pH. They do so over a range of pH from two to three units. This is called pH range which vary for different indicators.

Redox Reactions

Redox Reactions

When oxidation and reduction reactions take place simultaneously in a reaction then overall process is called redox reaction.

Oxidation

There are number of ways to define oxidation :

- It is the process in which electrons are lost from an atom or ion.
  e.g., $Na \rightarrow Na^+ + e^-$; $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
  $2Cl^- \rightarrow Cl_2 + 2e^-$; $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- Oxidation is a process which involves addition of oxygen *e.g.*, $C + O_2 \rightarrow CO_2$ (C is oxidised to CO_2)
  $2Mg + O_2 \rightarrow 2MgO$ (Mg is oxidised to MgO)
- Removal of hydrogen is also known as oxidation *e.g.*, $H_2S + Cl_2 \rightarrow 2HCl + S$ (H_2S is oxidised to S)
- Addition of any eletronegative element is called oxidation *e.g.*, $2Na + Cl_2 \rightarrow 2NaCl$ (Na is oxidised)
- Removal of any eletropositive element is termed as oxidation *e.g.*,
  $2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$
  (Removal of K oxidation of K_2MnO_4)

Reduction

Reduction is also defined in number of ways :

- It is the process in which an atom or ion gains one or more electrons *e.g.*,
  $Cl_2 + 2e^- \rightarrow 2Cl^-$
  $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$
- Reduction is a process which involves removal of oxygen *e.g.*,
  $CuO + H_2 \rightarrow Cu + H_2O$ (CuO is reduced to Cu)
- Addition of hydrogen is also known as reduction *e.g.*, $H_2 + Cl_2 \rightarrow 2HCl$ (Cl_2 is reduced to HCl)
  $Br_2 + H_2S \rightarrow 2HBr + S$ (Br_2 is reduced to HBr)
- Removal of any electronegative element is called reduction *e.g.*,
  $2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$ (Reduction of $FeCl_3$)
- Addition of electropositive element is termed as reduction *e.g.*,
  $HgCl_2 + Hg \rightarrow Hg_2Cl_2$ (Reduction of $HgCl_2$)

Oxidation Number

- Oxidation number of an element is defined as the charge which an atom of the element has on its ion or in combined state with other atoms.
- **Some rules for assigning oxidation number :**
  – The oxidation number of atoms of all the elements in the free state is zero.
  – For monatomic ions, the oxidation number of atom is equal to its charge.
  – The oxidation number of oxygen in most compounds is –2 except in peroxides (–1), superoxides (–1/2), oxygen difluoride, OF_2 (+2) and dioxygen difluoride, O_2F_2 (+1).
  – The oxidation number of hydrogen is +1, except in metal hydrides where it is –1.
  – Fluorine always has an oxidation number of –1.
  – The algebraic sum of oxidation numbers of all the atoms in a compound must be zero.
  – In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion is equal to the net charge on the ion.

Oxidising and Reducing Agents

- A substance which can gain electrons *i.e.*, undergoing reduction is known as oxidising agent or oxidant.
- A substance which can lose electrons *i.e.*, undergoing oxidation is known as reducing agent or reductant.
- **Some important oxidising and reducing agents :**

Oxidising agents	Reducing agents	Both reducing and oxidising agents
$KMnO_4$, $K_2Cr_2O_7$, $NaNO_3$, CrO_3, H_2SO_4, $KClO_3$, HNO_3, SO_3, $FeCl_3$, O_2, O_3, P_4O_{10}, etc.	Li, Cs, Na, Al, Fe, Zn, HCl, HBr, HI, H_2S, $FeCl_2$, $FeSO_4$, $SnCl_2$, Hg_2Cl_2, Cu_2O, NaH etc.	H_2O_2, SO_2, H_2SO_3, HNO_2, $NaNO_2$, Na_2SO_3, etc.

Equivalent weights of oxidising and reducing agents

- It can be defined as the molecular weight divided by the number of electrons gained or lost respectively as represented in the balanced chemical equation.

Equivalent weight of oxidant or reductant

$$= \frac{\text{Molecular weight}}{\text{No. of electrons gained or lost}}$$

or Equivalent weight of oxidant or reductant

$$= \frac{\text{Formula weight}}{\text{Total change in oxidation number}}$$

Types of Redox Reactions

- **Combination reactions :** These are the reactions in which two atoms or molecules combine together to form a third molecule. In these reactions at least one of the reactants must be in elemental form *e.g.*, $C + 2H_2 \longrightarrow CH_4$
- **Decomposition reactions :** These are the reactions in which a molecule or compound breaks down to form two or more atoms or molecules. These are simply reverse of combination reactions. For these reactions to be redox reaction one of the products must be in elemental form *e.g.*, $2KClO_3 \rightarrow 2KCl + 3O_2$
- **Displacement reactions :** These are the reactions in which an atom or ion in a compound is replaced by another atom or ion. These reactions are represented as
  $AB + C \rightarrow AC + B$
  Displacement reactions are further divided into two categories :
  - **Metal displacement reactions :** If a metal atom/ion is displaced by another metal atom/ion in the reaction, it is called metal displacement reaction *e.g.*,
    $$\overset{+4}{\mathbf{Ti}}\mathbf{Cl_4} + 2\overset{0}{\mathbf{Mg}} \rightarrow \overset{0}{\mathbf{Ti}} + 2\overset{+2}{\mathbf{Mg}}\mathbf{Cl_2}$$
    $$\overset{+2}{Cu}SO_4 + \overset{0}{Zn} \rightarrow \overset{0}{Cu} + \overset{+2}{Zn}SO_4$$
  - **Non-metal displacement reactions :** If a non-metal atom/ion is displaced by a metal atom/ion in the reaction, the reaction is called non-metal displacement reaction *e.g.*,
    $$\overset{0}{Zn} + \overset{+1}{H_2}SO_4 \rightarrow \overset{+2}{Zn}SO_4 + \overset{0}{H_2}$$
    $$2\overset{0}{Al} + 3\overset{+1}{H_2}O \rightarrow \overset{+3}{Al_2}O_3 + 3\overset{0}{H_2}$$
- **Disproportionation reactions :** These are the reactions in which a single species is oxidised as well as reduced simultaneously. In these reactions, the reacting species must have an element which can have at least three variable oxidation states.

Reduced

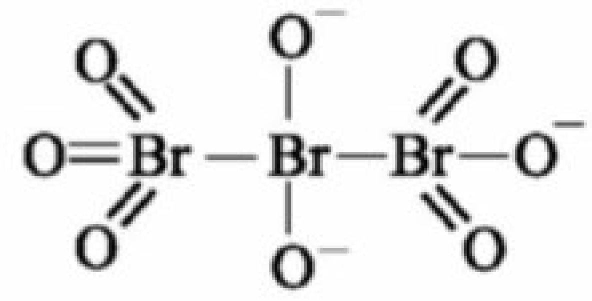
$$3\overset{+3}{ClO_2^-} \longrightarrow \overset{-1}{Cl^-} + 2\overset{+5}{ClO_3^-}$$

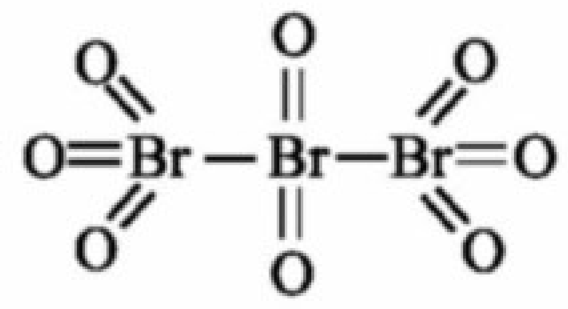
Oxidised

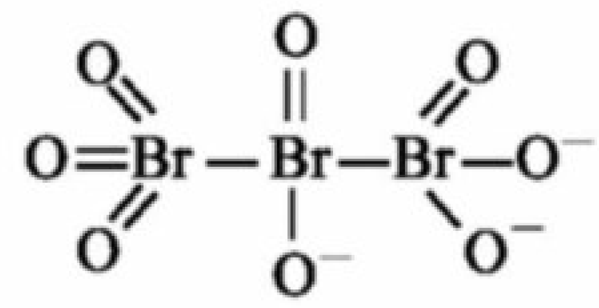
PEEP INTO PREVIOUS YEARS

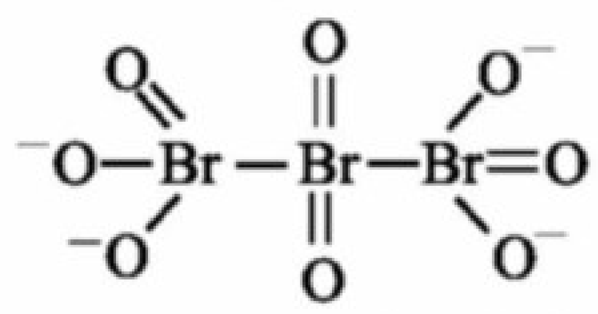
7. An example of a disproportionation reaction is
   (a) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
   (b) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$
   (c) $2CuBr \rightarrow CuBr_2 + Cu$
   (d) $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$
   (JEE Main 2019)

8. The correct structure of tribromooctaoxide is

   (a) 

   (b) 

   (c) 

   (d) 

   (NEET 2019)

9. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?
   (a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
   (b) $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
   (c) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
   (d) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$
   (NEET-II 2016)

Balancing of Redox Reactions

Redox reactions can be balanced by two methods :

- **Oxidation number method :** This method involves the following steps :
  Step 1 : Write the skeleton redox reaction.
  Step 2 : Identify elements undergoing oxidation or reduction and write the oxidation number of atoms above the symbol.
  Step 3 : Balance, increase in oxidation number and decrease in oxidation number by multiplying the oxidant and reductant with suitable integers.

Step 4 : Balance the atoms other than hydrogen and oxygen.

Step 5 : Balance hydrogen and oxygen.

- **Acidic medium :** Add H_2O to balance O and then add H^+ to balance H atoms.
- **Basic medium :** Add OH^- to balance charge and then add H_2O to balance H and O atoms to the other side.

- **Half reaction method :** This method involves the following steps :

  Step 1 : Write down the equation in ionic form.

  Step 2 : Split the reaction into two half reactions; one for oxidation and other for reduction.

  Step 3 : Balance each half reaction by using the following rules :
  - First balance the atoms which undergo oxidation or reduction.
  - Balance the atoms other than hydrogen and oxygen using simple multiples.
  - **In acidic and neutral solution :** Add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen.
  - **In basic medium :** For each excess of oxygen add H_2O to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess of hydrogen on same side and one water molecule to the other side.

  Step 4 : Add electrons to the side deficient in electrons to balance charge.

  Step 5 : Multiply two half reactions by suitable integer to equalise number of electrons in both reactions.

  Step 6 : Add the two half reaction to achieve the overall reaction and cancel the electrons on each side.

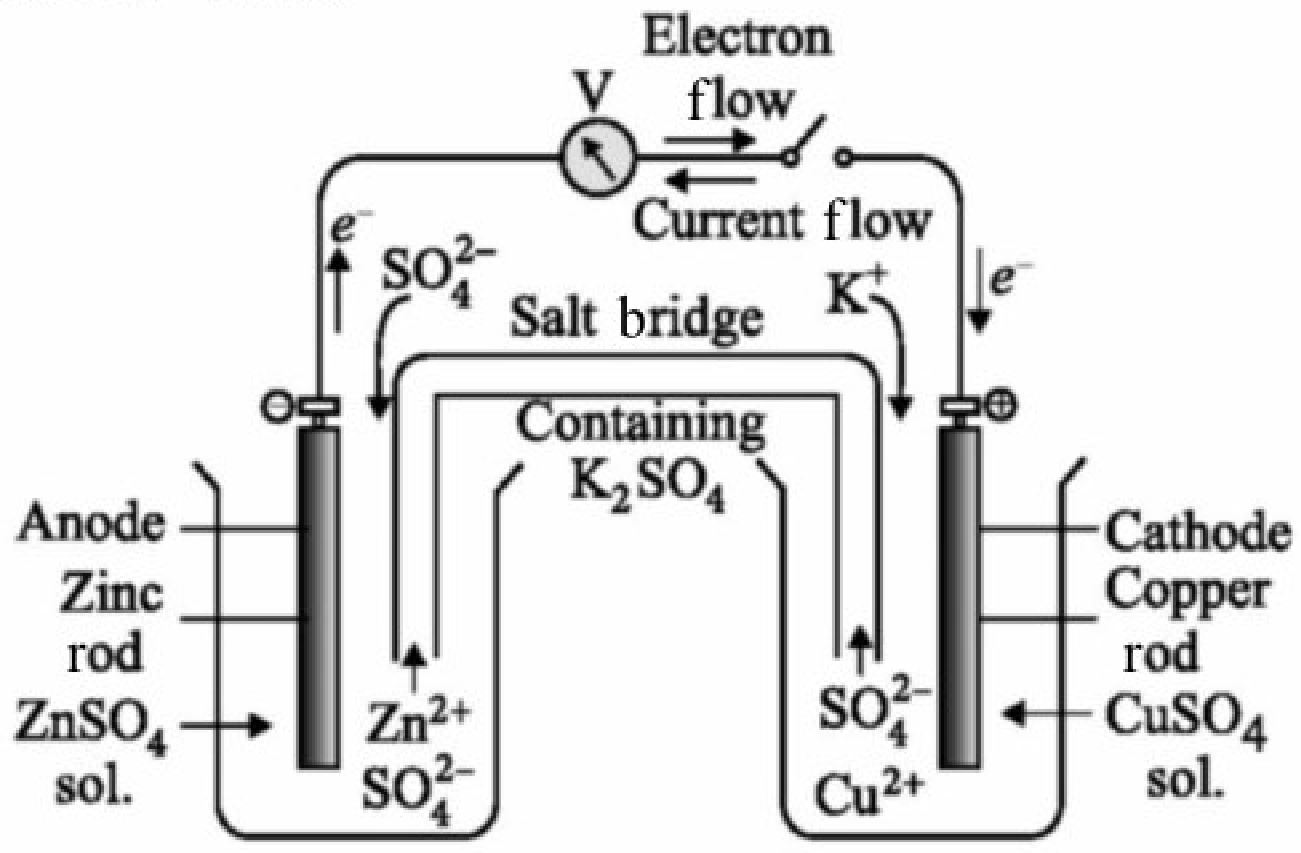
Redox Titrations

The method is used to determine the strength of a reductant/oxidant using a redox sensitive indicators.

- If the reagent itself is intensely coloured *e.g.*, MnO_4^-, it can act as self-indicator.
- If there is no auto-colour change, there are indicators which are oxidised immediately after the last drop of the reactant has reacted, producing a dramatic colour change *e.g.*, $Cr_2O_7^{2-}$ oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.
- Starch is used as indicator in case of those reagents which can either oxidise I^- ions such as Cu^{2+} or reduce I_2 such as $S_2O_3^{2-}$ ions as it gives intense blue colour with molecular iodine.

Redox Reactions and Electrode Processes

- **Redox couple :** It is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half-reaction. For example, a redox couple is represented as Zn^{2+}/Zn and Cu^{2+}/Cu ;



- **Salt bridge :** It completes the circuit and used to maintain electrical neutrality.
- **Electrode potential :** The potential difference set up between the metal and its own ions in the solution is called electrode potential. In general, it is the tendency of an electrode to gain or lose electrons.
- **Standard electrode potential ($E°$) :** If the concentration of each species taking part in the electrode reaction is unity and the reaction is carried out at 298 K, then the potential of each electrode is called standard electrode potential.
  - Standard electrode potential of hydrogen is taken as 0.00 volts by convention.
  - **Electrochemical series :** It is a series in which a list of oxidising agents are arranged in decreasing order of their strength. It is also called activity or electromotive series.
  - A negative $E°$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
  - A positive $E°$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Redox Reactions in Everyday Life

- Energy required for daily needs obtained from fuel oxidation.

- In extraction of metal, metals are obtained by using suitable reducing agent *e.g.*, coke is used in blast furnace for obtaining iron from Fe_2O_3 as,
  $Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)}$
- A breathalyzer test for alcohol makes use of the oxidation of alcohol by dichromate ion which is a redox reaction. The dichromate ion is orange but its reduction product is green Cr^{3+} ion. The breath of a person who has drunk, contains alcohol vapour, which passess through an acidic solution containing $Cr_2O_7^{2-}$, when the person blows through the breathalyzer device, any alcohol in the exhaled air is oxidised, which is signaled by the appearance of green Cr^{3+}. The more alcohol the person has consumed, the greater the intensity of the green colour.

Peep Into Previous Years

10. Consider the following reduction processes :
$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$; $E° = -0.76$ V
$Ca^{2+} + 2e^- \rightarrow Ca_{(s)}$; $E° = -2.87$ V
$Mg^{2+} + 2e^- \rightarrow Mg_{(s)}$; $E° = -2.36$ V
$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$; $E° = -0.25$ V
The reducing power of the metals increases in the order
(a) Ca < Zn < Mg < Ni (b) Ca < Mg < Zn < Ni
(c) Zn < Mg < Ni < Ca (d) Ni < Zn < Mg < Ca
(JEE Main 2019)

11. The standard (reduction) electrode potentials for metal-metal ion (M/M^{2+}) electrodes *P*, *Q*, *R* and *S* are respectively – 0.44 V, + 0.34 V, – 0.76 V and – 0.25 V. The increasing order of their reducing capacities is
(a) $P < R < S < Q$ (b) $Q < S < P < R$
(c) $Q < S < R < P$ (d) $P < R < Q < S$
(J & K CET 2019)

12. For the redox reaction,
$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$
The correct coefficients of the reactants for the balanced equation are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	16	5	2
(b)	2	5	16
(c)	2	16	5
(d)	5	16	2

(NEET 2018)

Points For Extra Scoring

- Metals generally exhibit positive oxidation states whereas the oxidation state in case of non-metals may be positive or negative. Moreover, transition elements exhibit variable oxidation states.
- The reverse of disproportionation reaction is called comproportionation reaction in which two reactants each having the same element but in different oxidation states will form a product in which the oxidation state of its both the atoms is similar, *e.g.*, reaction occurring in lead storage battery.

$$\overset{0}{Pb}_{(s)} + \overset{+4}{Pb}O_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2\overset{+2}{Pb}SO_{4(s)} + 2H_2O_{(l)}$$

- The salt bridge contains only those electrolytes for which the ionic mobilities of cations and anions are nearly the same.
- Lower the electrode potential, stronger is the reducing agent.
- Higher the electrode potential, stronger is the oxidising agent.
- For a disproportionation reaction, equivalent mass of oxidant/reductant = sum of equivalent mass of two half-reactions.

e.g. $4H_3\overset{(+3)}{P}O_3 \rightarrow 3H_3\overset{(+5)}{P}O_4 + \overset{(-3)}{P}H_3$

Eq. mass of $H_3PO_3 = \frac{M}{2} + \frac{M}{6} = \frac{2M}{3}$

Answer Key For Peep Into Previous Years

1.	(b)	**2.**	(a)	**3.**	(a)	**4.**	(d)	**5.**	(d)	**6.**	(a)
7.	(c)	**8.**	(b)	**9.**	(d)	**10.**	(d)	**11.**	(b)	**12.**	(b)

WRAP it up!

1. Consider the following reactions in which all the reactants and the products are in gaseous state.

$2PQ \rightleftharpoons P_2 + Q_2$; $K_1 = 2.5 \times 10^5$

$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR$; $K_2 = 5 \times 10^{-3}$

The value of K_3 for the equilibrium,

$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$, is

(a) 2.5×10^{-3} (b) 2.5×10^3
(c) 1.0×10^{-5} (d) 5×10^3

2. For the reaction, $X_{(g)} + Y_{(g)} \rightleftharpoons 3Z_{(g)}$ at 25°C, a 3 litre vessel contains 1, 2 and 4 moles of X, Y and Z respectively. Identify the correct statement.
(a) The reaction will occur in forward direction if K_c for the reaction is 10.
(b) The reaction will occur in backward direction if K_c for the reaction is 15.
(c) The reaction will be at equilibrium if K_c for the reaction is 10.66.
(d) All of the above.

3. 5 g mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M $KMnO_4$ in acidic medium. The percentage of $FeSO_4 \cdot 7H_2O$ in mixture is
(a) 15.29 (b) 30.58 (c) 20.24 (d) 25.29

4. How much volume of 0.3 M NH_4OH should be added to 30 mL of 0.2 M solution of NH_4Cl to obtain a buffer solution of pH 10.
[Given, pK_b for NH_4OH = 4.75]
(a) 130.7 mL (b) 225 mL
(c) 112.5 mL (d) 109.5 mL

5. The correct sequence of the oxidation state of underlined elements is

$Na\underline{B}H_4$, $K_2\underline{Ta}F_7$, $Mg_2\underline{P}_2O_7$, $Na_2\underline{S}_4O_6$, $\underline{N}_3H$

(a) +3, +5, +5, +2.5, $-\frac{1}{3}$ (b) +5, +3, +5, +3, $+\frac{1}{3}$
(c) +3, +3, +5, +5, $-\frac{1}{3}$ (d) +5, +5, +3, +2.5, $+\frac{1}{3}$

6. What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N hydrochloric acid assuming complete ionization of the acid and base?
(a) 12.301 (b) 2.699 (c) 10.546 (d) 11.477

7. What is the % dissociation of H_2S, if 1 mole of H_2S is introduced in one litre vessel at 1000 K?
K_c for the reaction,
$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 1×10^{-6}.
(a) 1.67% (b) 1.3% (c) 1.58% (d) 0.01%

8. In the disproportionation reaction,
$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$, the equivalent mass of the oxidizing agent is
(Molar mass of $HClO_3$ = 84.45)
(a) 16.89 (b) 32.22 (c) 84.45 (d) 28.15

9. An element A in a compound ABD has oxidation number A^{n-}. It is oxidised by $Cr_2O_7^{2-}$ in acidic medium. In the experiment 1.68×10^{-3} mole of $K_2Cr_2O_7$ were used for 3.26×10^{-3} mole of ABD. The new oxidation number of A after oxidation is
(a) 3 (b) $3 - n$ (c) $n - 3$ (d) $+n$.

10. For the following reaction,
$CH_3COCH_{3(g)} \rightleftharpoons CH_3CH_{3(g)} + CO_{(g)}$; when 1 mole of $CH_3COCH_{3(g)}$ is taken, initial pressure of CH_3COCH_3 is 100 mm of Hg. When equilibrium is set up, mole fraction of $CO_{(g)}$ is 1/3, hence K_p is
(a) 100 mm Hg (b) 50 mm Hg
(c) 25 mm Hg (d) 150 mm Hg.

11. The degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.
(a) 2 atm (b) 0.225 atm
(c) 0.12 atm (d) 2.50 atm

12. The oxidation states of sulphur in Caro's and Marshall's acid are
(a) +6, +6 (b) +4, +6 (c) +6, −6 (d) +6, +4

13. In which of the following reactions, H_2O_2 acts as a reducing agent?
(i) $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
(ii) $H_2O_2 - 2e^- \longrightarrow O_2 + 2H^+$
(iii) $H_2O_2 + 2e^- \longrightarrow 2OH^-$
(iv) $H_2O_2 + 2OH^- - 2e^- \longrightarrow O_2 + 2H_2O$
(a) (ii), (iv) (b) (i), (ii) (c) (iii), (iv) (d) (i), (iii)

14. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (M.wt. = 283 g/mol), the equilibrium which sets in is

$AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution?

(a) 1.0×10^{-4} g (b) 28.3×10^{-2} g
(c) 2.83×10^{-3} g (d) 1.0×10^{-7} g

15. 3.92 g of ferrous ammonium sulphate are dissolved in 100 mL water. 20 mL of this solution requires 18 mL of potassium permanganate during titration for complete oxidation. The weight of $KMnO_4$ present in one litre of the solution is

(a) 34.76 g (b) 12.38 g (c) 1.238 g (d) 3.51 g

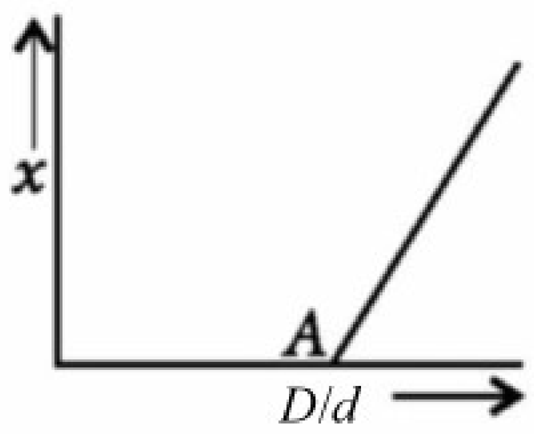
16. At a certain temperature, the equilibrium constant K_c is 16 for the reaction,

$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$

If 1.0 mol each of all the four gases is taken in a one litre container then the concentration of NO_2 at equilibrium would be

(a) 1.6 mol L^{-1} (b) 0.8 mol L^{-1}
(c) 0.4 mol L^{-1} (d) 0.6 mol L^{-1}.

17. Before equilibrium is set-up for the chemical reaction, $N_2O_4 \rightleftharpoons 2NO_2$, vapour density of the gaseous mixture was measured. If D is the theoretical value of vapour density, variation of x with D/d is shown by the following graph.



What is the value of D/d at point A?

(a) 0 (b) 1.5 (c) 1 (d) 0.5

18. The standard reduction potentials of Mg, Zn, Ni, H_2, Cu and Ag are –2.37, – 0.76, – 0.25, 0.00, 0.34 and 0.80 volt respectively. Which one of the following cells has maximum voltage?

(a) $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$
(b) $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$
(c) $Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$
(d) $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

19. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?

(a) – 4 (b) 0 (c) + 4 (d) + 6

20. On adding 0.1 M solution each of Ag^+, Ba^{2+}, Ca^{2+} in a Na_2SO_4 solution, which species is first precipitated?

$[K_{sp}(BaSO_4) = 10^{-11}, K_{sp}(CaSO_4) = 10^{-6}, K_{sp}(Ag_2SO_4) = 10^{-5}]$

(a) Ag_2SO_4 (b) $BaSO_4$
(c) $CaSO_4$ (d) All of these

SOLUTIONS

1. (c) : $2PQ \rightleftharpoons P_2 + Q_2;\ K_1 = \dfrac{[P_2][Q_2]}{[PQ]^2} = 2.5 \times 10^5$

$$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR\ ;\ K_2 = \frac{[PQR]}{[PQ][R_2]^{1/2}} = 5 \times 10^{-3}$$

$$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$$

$$K_3 = \frac{[PQR]}{[P_2]^{1/2}[Q_2]^{1/2}[R_2]^{1/2}} = \frac{K_2}{\sqrt{K_1}} = \frac{5 \times 10^{-3}}{\sqrt{2.5 \times 10^5}}$$

$= 1 \times 10^{-5}$

2. (c) : $X_{(g)} + Y_{(g)} \rightleftharpoons 3Z_{(g)}$

$[X] = 1/3, [Y] = 2/3, [Z] = 4/3$

$$\Rightarrow Q_c = \frac{\left(\frac{4}{3}\right)^3}{\left(\frac{1}{3}\right)\left(\frac{2}{3}\right)} = 10.66$$

(a) Since, $K_c = 10$ *i.e.* $Q_c > K_c$, thus reaction will occur in backward direction.

(b) Since, $K_c = 15$ *i.e.* $K_c > Q_c$, thus the reaction will occur in forward direction.

(c) Since, $Q_c = K_c$, reaction is at equilibrium.

3. (a) : $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$; $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$M_{eq.}$ of $KMnO_4$ = $M_{eq.}$ of $FeSO_4 \cdot 7H_2O$

$$5.5 \times 0.1 \times 5 = \frac{w}{278} \times 1000 \quad \therefore\ w = 0.7645$$

$$\therefore\ \%\ \text{of}\ FeSO_4 \cdot 7H_2O = \frac{0.7645}{5} \times 100 = 15.29\%$$

4. (c) : We know, pH + pOH = 14

$\therefore$ pOH of the buffer = 14 – 10 = 4

For basic buffers, $pOH = pK_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}$

$$4 = 4.75 + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

or $\log\dfrac{[\text{Salt}]}{[\text{Base}]} = -0.75 \Rightarrow \dfrac{[\text{Salt}]}{[\text{Base}]} = 0.1778$

or $\dfrac{\frac{0.2}{1000} \times 30}{\frac{0.3}{1000} \times V} = 0.1778 \quad \therefore\ V = 112.5$ mL

5. (a) : $Na\underline{B}H_4 : +1 + x + 4(-1) = 0 \Rightarrow x = +3$

$K_2\underline{Ta}F_7 : +2 + x + (-7) = 0 \Rightarrow x = +5$

$Mg_2\underline{P}_2O_7 : +4 + 2x + (-14) = 0 \Rightarrow x = +5$
$Na_2\underline{S}_4O_6 : +2 + 4x + (-12) = 0$
or $4x = 10 \Rightarrow x = +2.5$

$N_3H : 3x + 1 = 0 \Rightarrow x = -\frac{1}{3}$

6. (a) : Moles of NaOH $= \frac{800 \times 0.05}{1000} = 0.04$

Moles of HCl $= \frac{200 \times 0.1}{1000} = 0.02$

	$NaOH$	$+ HCl \longrightarrow$	$NaCl$	$+ H_2O$
Initial moles :	0.04	0.02	0	0
Moles after reaction :	0.02	0	0.02	0.02

Total volume of solution = 800 + 200 = 1000 mL = 1L

$[OH^-] = \frac{0.02}{1} = 0.02$

pOH = $-\log(2 \times 10^{-2})$
pOH = 1.699
pH = 14 – 1.699 = 12.301

7. (b) : $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$

	$2H_2S_{(g)}$	$2H_{2(g)}$	$S_{2(g)}$
Initial moles :	1	0	0
Moles at equilibrium :	$(1-\alpha)$	α	$\alpha/2$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\alpha^2(\alpha/2)}{(1-\alpha)^2} \quad (\because \alpha <<< 1)$$

$$K_c = \frac{\alpha^3}{2} \Rightarrow 1 \times 10^{-6} = \frac{\alpha^3}{2}$$

$\alpha^3 = 2 \times 10^{-6}$
$\alpha = (2 \times 10^{-6})^{1/3} = 1.2599 \times 10^{-2} \simeq 1.3 \times 10^{-2}$

% dissociation = $1.3 \times 10^{-2} \times 100 = 1.3\%$

8. (a) : $\overset{+5}{ClO_3^-} \longrightarrow \overset{0}{Cl_2}$
$x - 6 = -1$ $\quad x = 0$
$x = +5$ $\quad x = 0$

Oxidation number has changed by 5

Equivalent mass $= \frac{\text{Molecular mass}}{\text{Change in oxidation number}} = \frac{84.45}{5}$
$= 16.89$

9. (b) : $A^{n-} \longrightarrow A^{a+} + (a+n)e^-$

$\overset{6+}{Cr_2} + 6e^- \longrightarrow 2Cr^{3+}$

Also $M_{eq.}$ of A = $M_{eq.}$ of $K_2Cr_2O_7$
$3.26 \times 10^{-3}(a+n) = 1.68 \times 10^{-3} \times 6$
or $a + n = 3 \Rightarrow a = 3 - n$

10. (b) : $CH_3COCH_{3(g)} \rightleftharpoons CH_3CH_{3(g)} + CO_{(g)}$

	$CH_3COCH_{3(g)}$	$CH_3CH_{3(g)}$	$CO_{(g)}$
Initial :	1	0	0
At eq. :	$(1-x)$	x	x

Total moles at equilibrium : $(1 + x)$

$$x_{CO} = \frac{x}{1+x} = \frac{1}{3} \qquad \therefore x = 0.5$$

$\therefore$ Total moles at equilibrium = 1.5
$\because$ Initial pressure = 100 mm of Hg

$$\frac{P_1}{n_1} = \frac{P_2}{n_2} \Rightarrow \frac{100}{1} = \frac{P_2}{1.5}$$

$\therefore$ Equilibrium pressure = 150 mm of Hg
$p_{CO} = x_{CO} \cdot p_T \Rightarrow 50$ mm of Hg
$p_{CH_3CH_3} = x_{CH_3CH_3} \cdot p_T \Rightarrow 50$ mm of Hg
$p_{CH_3COCH_3} = x_{CH_3COCH_3} \cdot p_T \Rightarrow 50$ mm of Hg

$$K_p = \frac{p_{CH_3CH_3} \cdot p_{CO}}{p_{CH_3COCH_3}} = 50 \text{ mm of Hg}$$

11. (c) : If α is the degree of dissociation at certain temperature under the atmospheric pressure, then

	$PCl_5 \rightleftharpoons$	PCl_3	$+ Cl_2$
Initial conc. :	1	0	0
At equilibrium :	$1-\alpha$	α	α

Now, $K_p = \frac{\alpha^2}{1-\alpha^2}P$

Putting $P = 1$ atm and $\alpha = 0.2$

$$K_p = \frac{(0.2)^2}{1-(0.2)^2} \times 1 = 0.04$$

When $\alpha = \frac{1}{2} = 0.5$, then let pressure is P'

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P' \Rightarrow 0.04 = \frac{(0.5)^2 P'}{1-(0.5)^2}$$

$$P' = \frac{(0.04)[1-(0.5)^2]}{(0.5)^2} = 0.12 \text{ atm}$$

12. (a)

13. (a) : The reducing agent itself gets oxidised *i.e.*, the oxidation number increases.

(1) $\overset{-1}{H_2O_2} + 2H^+ + 2e^- \longrightarrow 2\overset{-2}{H_2O}$

(2) $\overset{-1}{H_2O_2} - 2e^- \longrightarrow \overset{0}{O_2} + 2H^+$

(3) $\overset{-1}{H_2O_2} + 2e^- \longrightarrow 2\overset{-2}{OH^-}$

(4) $\overset{-1}{H_2O_2} + 2OH^- - 2e^- \longrightarrow \overset{0}{O_2} + 2H_2O$

14. (c) : $AgIO_3 \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{IO_3^-}$ [s = Solubility]

$K_{sp} = s^2$

or, $s^2 = 1.0 \times 10^{-8}$ or, $s = 1.0 \times 10^{-4}$ mol/L
$= 1.0 \times 10^{-4} \times 283$ g/L $\quad (\because 1 \text{ mol } AgIO_3 = 283 \text{ g})$

$\because$ 1 L or 1000 mL contain $1.0 \times 10^{-4} \times 283$ g of $AgIO_3$

$$\therefore \quad 100 \text{ mL} = \frac{1.0\times10^{-4}\times283}{1000}\times100$$

$$= \frac{1.0\times10^{-4}\times283\times100}{1000} \text{ g/100mL}$$

$= 28.3 \times 10^{-4}$ g/100 mL $= 2.83 \times 10^{-3}$ g/100 mL

15. (d): The redox reaction involving the oxidation of Fe^{2+} (from ferrous ammonium sulphate) is

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Mol. wt. of ferrous ammonium sulphate,

$FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O = 392$

$\therefore$ Molarity of $FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O$

$$= \frac{\text{Wt.}}{\text{Mol. wt.}}\times\frac{1000}{\text{Volume}} = \frac{3.92}{392}\times\frac{1000}{100} = 0.1$$

Applying molarity equation,

$$\frac{M_1V_1}{n_1}\text{(Ferrous ammonium sulphate)} = \frac{M_2V_2}{n_2}(KMnO_4)$$

$$\text{or,}\quad \frac{0\cdot1\times20}{5} = \frac{M_2\times18}{1} \quad\text{or}\quad M_2 = \frac{0\cdot1\times20}{5\times18} = \frac{1}{45}$$

Amount of $KMnO_4$ present in one litre

$$= \text{Molarity}\times\text{Mol. wt.}(KMnO_4) = \frac{1}{45}\times158 = 3\cdot51 \text{ g}$$

16. (c) :

	$SO_{2(g)}$ +	$NO_{2(g)}$ $\rightleftharpoons$	$SO_{3(g)}$ +	$NO_{(g)}$
Initial conc.	1	1	1	1
At equilibrium	$1-x$	$1-x$	$1+x$	$1+x$

$$K_c = \frac{[SO_3][NO]}{[SO_2]\,[NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \quad\text{or}\quad x = 0.6$$

$[NO_2] = 1 - x = 1 - 0.6 = 0.4$ mol L^{-1}

17. (c) : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Degree of dissociation, $\alpha = \dfrac{D-d}{d}$ or $\alpha = \dfrac{D}{d} - 1$

At A, $\alpha = 0$

$$\therefore \quad \frac{D}{d} - 1 = 0 \quad\text{or}\quad \frac{D}{d} = 1$$

18. (a) : $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$

$E^\circ_{cell} = E_c - E_a = 0.80 - (-2.37) = +3.17$ V

$Cu^{2+} + H_2 \rightarrow Cu + 2H^+$

$E^\circ_{cell} = 0.34 - 0.00 = +0.34$ V

$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$

$E^\circ_{cell} = 0.34 - (-0.25) = 0.59$

$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$E^\circ_{cell} = 0.80 - (-0.76\text{ V}) = 1.56$ V

19. (d):

Element	%	At. mass	Relative number of moles	Simplest ratio
Xe	53.5	131	0.408	1
F	46.5	19	2.44	6

$\therefore$ The empirical formula is XeF_6.

$\therefore$ Oxidation state of Xe is +6.

20. (b): For Ag_2SO_4; $K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$

$\therefore$ $[SO_4^{2-}]$ needed for precipitation of

$$Ag_2SO_4 > \frac{K_{sp}}{[Ag^+]^2} = \frac{10^{-5}}{0.1\times0.1} = 10^{-3}\text{M}$$

$SO_4^{2-} > 10^{-3}$ M

For $CaSO_4$; $K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$

$\therefore$ $[SO_4^{2-}]$ needed for precipitation of

$$CaSO_4 > \frac{K_{sp}}{[Ca^{2+}]} = \frac{10^{-6}}{0.1} = 10^{-5}\text{M}$$

$$\text{For } BaSO_4\text{ ; } K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = \frac{10^{-11}}{0.1} = 10^{-10}$$

$\therefore$ $SO_4{}^{2-}$ needed for precipitation of $BaSO_4 > \dfrac{K_{sp}}{[Ba^{2+}]}$

$SO_4^{2-} > 10^{-10}$ M

Thus, minimum $[SO_4^{2-}]$ is required for precipitation of $BaSO_4$ and hence it is precipitated out first.

CBSE warm-up!

CLASS-XI

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 4 — Equilibrium | Redox Reactions

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Section A : Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
(iii) Section B : Q. no. 21 to 27 are short answer questions and carry 2 marks each.
(iv) Section C : Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
(v) Section D : Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
(vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
(vii) Use log tables if necessary, use of calculators is not allowed.

SECTION - A

1. A compound contains atoms X, Y and Z. The oxidation number of X is +2, Y is +5 and Z is −2. The possible formula of the compound is
(a) XYZ_2 (b) $Y_2(XZ_3)_2$
(c) $X_3(YZ_4)_2$ (d) $X_3(Y_4Z)_2$

2. The dissociation constants for acetic acid and HCN at 25 °C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the reaction,
$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$
would be
(a) 3.0×10^{-5} (b) 3.0×10^{-4}
(c) 3.0×10^{4} (d) 3.0×10^{5}

3. The equilibrium constant (K_c) for the reaction $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ at temperature T is 4×10^{-4}. The value of K_c for the reaction,
$NO_{(g)} \rightarrow \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$ at the same temperature is
(a) 2.5×10^{2} (b) 4×10^{-4}
(c) 50.0 (d) 0.02

4. Equivalent weight of MnO_4^- in acidic, basic and neutral medium are in the ratio of
(a) 3 : 5 : 15 (b) 5 : 3 : 1
(c) 5 : 1 : 3 (d) 3 : 5 : 5

5. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be
(a) 3.98×10^{8} (b) 3.88×10^{6}
(c) 3.68×10^{-6} (d) 3.98×10^{-6}

6. The brown ring complex compound is formulated as $[Fe(H_2O)_5NO]SO_4$. The oxidation state of Fe is
(a) +1 (b) +2 (c) +3 (d) zero

7. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is
(a) not a buffer solution with pH < 7
(b) not a buffer solution with pH > 7
(c) a buffer solution with pH < 7
(d) a buffer solution with pH > 7.

8. Amongst the following identify the species with an atom in +6 oxidation state.
(a) MnO_4^- (b) $[Cr(CN)_6]^{3-}$
(c) $[NiF_6]^{2-}$ (d) CrO_2Cl_2

9. The Henderson's equation for acetic acid and sodium acetate buffer is given by the expression
(a) $pH = pK_a - \log \frac{[CH_3COONa]}{[CH_3COOH]}$
(b) $pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$
(c) $pOH = pK_a - \log \frac{[CH_3COONa]}{[CH_3COOH]}$
(d) $pOH = pK_a - \log \frac{[CH_3COOH]}{[CH_3COONa]}$

10. In the reaction,
$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$
(a) bromine is oxidised and carbonate is reduced
(b) bromine is reduced and water is oxidised
(c) bromine is neither oxidised and reduced
(d) bromine is both oxidised and reduced.

11. What does the equilibrium constant $K < 1$ show?

12. K_c for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 0.5 mol^{-2} L^2 at 400 K. Find K_p. (Given R = 0.0821 litre atm deg^{-1} mol^{-1}).

13. Calculate the oxidation number of phosphorus in the following species :
(a) HPO_3^{2-} (b) PO_4^{3-}

14. Write down the conjugate base of $[Al(H_2O)_6]^{3+}$.

15. Calculate the oxidation number of nitrogen in nitrous acid and nitric acid.

16. The reaction quotient of a reversible reaction is Q_c and the equilibrium constant is K_c. What do you conclude from the reaction if $Q_c < K_c$?

17. A tank is full of water. Water is coming in as well as going out at the same rate. What will happen to the level of water in the tank? What is the name given to such state?

18. Is it possible to get precipitate of $Fe(OH)_3$ at pH = 2?

19. In the given reaction, identify the species undergoing oxidation and reduction :
$2HgCl_{2(aq)} + SnCl_{2(aq)} \longrightarrow Hg_2Cl_{2(s)} + SnCl_{4(aq)}$

20. Write the expression for the equilibrium constant K_c for the following equilibrium :
$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

SECTION - B

21. The value of K_w is 9.55 × 10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

22. The value of K_c for the reaction,
$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ is 1×10^{-4}.
At a given time, the composition of reaction mixture is
$[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol. In which direction will the reaction proceed?

23. Write chemical reaction to justify that hydrogen peroxide can act as oxidizing as well as reducing agent.

24. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

OR

Which of the following are oxidising agents and reducing agents? Justify your answer with half equations. Br_2, Fe^{3+}, I^-, Na.

25. Balance the following equation in basic medium by ion-electron method :
$Cl_2O_{7(g)} + H_2O_{2(aq)} \longrightarrow ClO^-_{2(aq)} + O_{2(g)}$
(KVS, NCT 2011)

26. Urine has a pH of 6.0. If a patient eliminates 1300 mL of urine per day, how many gram equivalents of the acid he eliminates per day?

OR

(i) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl. Why?
(ii) Calculate the pH of 2 g of TlOH dissolved in water to give 2 L of solution (At. mass of Tl = 204.384).

27. An iron rod is immersed in a solution containing 1.0 M $NiSO_4$ and 1.0 M $ZnSO_4$. Predict giving reasons which of the following reactions is likely to proceed :
(i) Fe reduces Zn^{2+} ions
(ii) Fe reduces Ni^{2+} ions
(Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V and $E^\circ_{Ni^{2+}/Ni} = -0.25$ V)

SECTION - C

28. Balance the following equation by oxidation number method.

$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

29. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in g L^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u).

OR

At 473 K, equilibrium constant K_c for the decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as :

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}; \Delta_r H° = 124.0$ kJ mol^{-1}

(i) What is the value of K_c for the reverse reaction at the same temperature?

(ii) What would be the effect on K_c if **(a)** the pressure is increased **(b)** the temperature is increased?

30. Is it possible to store :

(i) copper sulphate solution in a zinc vessel?

(ii) copper sulphate solution in a silver vessel?

(iii) copper sulphate solution in a gold vessel?

(Given : $E°_{Cu^{2+}/Cu} = +0.34$ V; $E°_{Zn^{2+}/Zn} = -0.76$ V; $E°_{Ag^+/Ag} = +0.80$ V and $E°_{Au^{3+}/Au} = +1.40$ V)

31. Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? (For copper iodate, $K_{sp} = 7.4 \times 10^{-8}$)

32. Determine the pH of 10^{-8} M HCl solution. (log 11 = 1.0414). *(KVS 2016, NCT 2016, 2017)*

OR

(a) The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is its pH? (log 3.8 = 0.58)

(NCERT, KVS 2008, NCT 2014)

(b) State Le-Chatelier's principle.

(NCT 2015, KVS 2016)

33. Both $Cr_2O^{2-}_{7(aq)}$ and $MnO^-_{4(aq)}$ can be used to titrate $Fe^{2+}_{(aq)}$. If in a given titration, 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ were used, then what volume of 0.1 M MnO_4^- solution would have been used for the same titration?

34. Copper dissolves in dilute nitric acid but not in dilute HCl. Explain.

SECTION - D

35. Explain the following :

(i) It is not possible to determine the absolute value of single electrode potential.

(ii) Iron undergoes oxidation more readily than copper.

(iii) In an electrochemical cell, an electrode with lower electrode potential acts as a reducing agent.

(iv) When a copper rod is placed in silver nitrate solution, the solution becomes hot but the reverse is not true.

(v) Iron reacts with dilute H_2SO_4 to evolve H_2 gas but Ag does not.

OR

Write the following redox reactions using half equations :

(i) $Zn_{(s)} + PbCl_{2(aq)} \longrightarrow Pb_{(s)} + ZnCl_{2(aq)}$

(ii) $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(s)} + 2Fe^{2+}_{(aq)}$

(iii) $2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$

(iv) $Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$

(v) $Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

In each of the reactions given above, mention

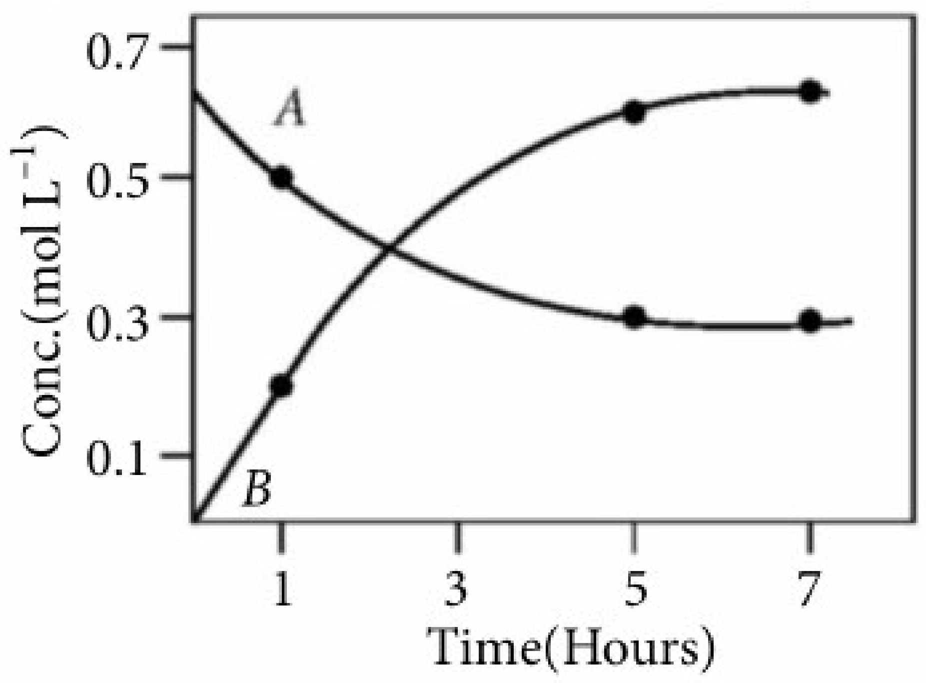
(a) which reactant is oxidized? To what?

(b) which reactant is the oxidiser?

(c) which reactant is reduced? To what?

(d) which reactant is the reducer?

36. **(i)** The progress of the reaction, $A \rightleftharpoons nB$, with time is represented in the following figure :



On the basis of above graph, determine :

(a) the value of n

(b) the equilibrium constant, K.

(ii) **(a)** Ammonium chloride is acidic in liquid ammonia solvent. Explain, why?

(b) Why does solubility of CO_2 decrease with rise in temperature?

OR

(i) A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl. (K_{sp} for $Ag_2CO_3 = 8.2 \times 10^{-12}$).

(ii) The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

37. (i) K_p for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 400 °C is 1.64×10^{-4} atm^{-2}. Find K_c. Also calculate $\Delta G°$ using K_p and K_c values.

(ii) Under what conditions, $K_c = K_p$ for a gaseous reactions? Give one example.

OR

(i) 0.15 mole of pyridinium chloride has been added to 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in the volume (K_b for pyridine $= 1.5 \times 10^{-9}$).

(ii) Describe the effect of **(a)** addition of H_2 **(b)** addition of CH_3OH **(c)** removal of CO **(d)** removal of CH_3OH, on the equilibrium of the reaction : $2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

SOLUTIONS

1. (c) : Sum of the oxidation numbers of atoms in it is zero.

2. (c) : Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5 \times 10^{-5}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} = 4.5 \times 10^{-10}$$

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$$

$$K = \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} \approx 0.3 \times 10^5 \text{ or } K = 3 \times 10^4$$

3. (c) : $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$; $K_c = 4 \times 10^{-4}$ ...(i)

On multiplying the equation (i) by $\frac{1}{2}$, we get

$\frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow NO_{(g)}$; K'_c ...(ii)

$$K'_c = \sqrt{K_c} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2}$$

On reversing the equation (ii), we get

$NO_{(g)} \rightarrow \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$; K''_c

$$K''_c = \frac{1}{K'_c} = \frac{1}{2 \times 10^{-2}} = 50.0$$

4. (d) : Acidic medium :

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Basic medium :

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Neutral medium :

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

If M is the molecular weight of $KMnO_4$, then its equivalent weights in acidic, basic, and neutral medium are respectively :

$$\frac{M}{5} : \frac{M}{3} : \frac{M}{3} \quad \text{or} \quad 3 : 5 : 5.$$

5. (d) : pH = – log[H^+]

[H^+] = antilog (–pH) = antilog(–5.4) = 3.98×10^{-6}

6. (a) : NO in iron complexes has oxidation number equal to one.

$x + 5 \times 0 + 1 - 2 = 0$, $\therefore$ $x = +1$.

7. (a) : HCl is a strong acid and its salt does not form buffer solution. As the resultant solution is acidic, hence pH is less than 7.

8. (d) : Oxidation numbers are

Mn in MnO_4^- is + 7

Cr in $[Cr(CN)_6]^{3-}$ is + 3 ($x - 6 = -3$ or $x = +3$)

Ni in $[NiF_6]^{2-}$ is + 4 ($x - 6 = -2$ or $x = +4$)

and Cr in CrO_2Cl_2 is +6 ($x + 2 \times (-2) + 2 \times (-1) = 0$

or $x - 4 - 2 = 0 \Rightarrow x = +6$.

9. (b)

10. (d) :

$$3\overset{0}{Br_2} + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + \overset{+5}{BrO_3^-} + 6HCO_3^-$$

Here, bromine is both oxidised and reduced

$\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-}$ (Reduction)

$\overset{0}{Br_2} \longrightarrow \overset{+5}{BrO_3^-}$ (Oxidation)

11. It shows that reaction is moving in backward direction. *i.e.*, it is far from completion.

12. $K_p = K_c (RT)^{\Delta n_g}$

$\Delta n_g = (n_P - n_R) = (2 - 4) = -2$

$K_p = 0.5 \times (0.082 \times 400)^{-2}$; $K_p = 4.648 \times 10^{-4}$ atm^{-2}

13. (a) $HPO_3^{2-} = +1 + x + (-6) = -2$ $\therefore$ $x = +3$

(b) $PO_4^{3-} = x + (-8) = -3$ $\therefore$ $x = +5$

14. $[Al(H_2O)_6]^{3+} \underset{\text{}}{\overset{H_2O}{\rightleftharpoons}} [Al(OH)(H_2O)_5]^{2+} + H_3O^+$
Acid Conjugate base

15. Nitrous acid *i.e.*, HNO_2
$+1 + x - 2 \times 2 = 0 ; x = +3$
Nitric acid *i.e.*, HNO_3
$+1 + x - 2 \times 3 = 0 ; x = +5$

16. If $Q_c < K_c$, the reaction tends towards forward direction to attain equilibrium.

17. It will remain same because rate of inflow is equal to rate of outflow. The state is called 'equilibrium'.

18. No, because $Fe(OH)_3$ will dissolve in strongly acidic medium.

Reduction

19. $2\overset{+2}{Hg}Cl_{2(aq)} + \overset{+2}{Sn}Cl_{2(aq)} \longrightarrow \overset{+1}{Hg_2}Cl_{2(s)} + \overset{+4}{Sn}Cl_{4(aq)}$

oxidation

$SnCl_2$ is oxidised and $HgCl_2$ is reduced.

20. $K_c = \dfrac{[H_{2(g)}]^4[Fe_3O_{4(s)}]}{[Fe_{(s)}]^3[H_2O_{(g)}]^4} = \dfrac{[H_{2(g)}]^4}{[H_2O_{(g)}]^4}$

($\because$ concentration of solids is taken as unity.)

21. $K_w = 9.55 \times 10^{-14}$
For water, $[H_3O^+] = [OH^-]$ and
$K_w = [H_3O^+]\,[OH^-] = 9.55 \times 10^{-14}$
or $[H_3O^+]\,[H_3O^+] = 9.55 \times 10^{-14}$
$[H_3O^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7}$ M
$pH = -\log(3.09 \times 10^{-7})$
$= -(\log 3.09 + \log 10^{-7}) = -(0.489 - 7) = 6.51$

22. $Q_c = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{(1 \times 10^{-5}) \times (1 \times 10^{-5})}{(2 \times 10^{-5})^2} = \dfrac{1}{4}$
$= 0.25 = 2.5 \times 10^{-1}$
Value of $K_c = 1 \times 10^{-4}$
Since $Q_c > K_c$, the reaction will proceed in reverse direction.

23. The O.N. of O in H_2O_2 is -1. It can increase its oxidation number to zero and acts as a reducing agent. It can also decrease its oxidation number to -2 and acts as an oxidising agent.

$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$
(H_2O_2 is acting as a reducing agent.)

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
(H_2O_2 is acting as an oxidising agent.)

24. In MnO_4^-, Mn has its highest oxidation state *i.e.*, +7. Hence, it does not undergo disproportionation reaction. MnO_4^{2-} has +6 oxidation state and can undergo disproportionation since it can adopt lower and higher oxidation state.

$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$
Manganate ion Permanganate ion

OR

$Br_2 + 2e^- \longrightarrow Br^-$: Reduction
(Oxidising agent)
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$: Reduction
(Oxidising agent)
$2I^- \longrightarrow I_2 + 2e^-$: Oxidation
(Reducing agent)
$Na \longrightarrow Na^+ + e^-$: Oxidation
(Reducing agent)

25. Oxidation half-reaction :
$H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)} + 2e^-] \times 4$ ...(i)
Reduction half-reaction :
$Cl_2O_{7(g)} + 3H_2O_{(l)} + 8e^- \rightarrow 2ClO^-_{2(aq)} + 6OH^-_{(aq)}$ ...(ii)
Adding eq. (i) and (ii)
$Cl_2O_{7(g)} + 4H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow$
$2ClO^-_{2(aq)} + 4O_{2(g)} + 5H_2O_{(l)}$

26. $\because$ pH = 6.0
$\therefore$ $[H_3O^+] = 10^{-6}$ M
i.e., $[\text{Acid}] = 10^{-6}$ M $= 10^{-6}$ N
Thus, 1000 mL of the urine contain acid $= 10^{-6}$ g eq.
$\therefore$ 1300 mL of the urine will contain acid $= 1.3 \times 10^{-6}$ g eq.

OR

(i) The solubility product of $Mg(OH)_2$ is high. Presence of NH_4Cl suppresses the dissociation of NH_4OH due to common ion effect thus giving low concentration of $[OH^-]$. The ionic product, therefore, cannot exceed the solubility product.

(ii) Molarity of TlOH

$= \dfrac{\text{Given mass}}{\text{Molecular mass}} \times \dfrac{1}{\text{Volume of solution (in litres)}}$

$= \dfrac{22}{221.38} \times \dfrac{1}{2} = 0.0045 \text{ mol L}^{-1}$

Assuming complete ionisation of TlOH,
$[OH^-] = 0.0045 \text{ mol L}^{-1}$
So, $[H^+] = K_w/[OH^-] = 2.22 \times 10^{-12}$
$pH = -\log [H^+] = 11.65$

27. **(i)** Since, $E°$ of Zn is more negative than that of Fe, therefore, Zn is more likely to be oxidised than Fe. In other words, Fe rod will not reduce Zn^{2+} ions.

(ii) Since, $E°$ of Fe is more negative than that of Ni, therefore, Fe will be oxidised to Fe^{2+} ions while Ni^{2+} ions will be reduced to Ni. Thus, Fe reduces Ni^{2+} ions.

28. $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

Change in oxidation number has occurred in chromium and iron.

$$\overset{+6}{K_2Cr_2O_7} \rightarrow \overset{+3}{Cr_2(SO_4)_3} \qquad ...(i)$$

$$\overset{+2}{2FeSO_4} \rightarrow \overset{+3}{Fe_2(SO_4)_3} \qquad ...(ii)$$

Decrease in oxidation number of Cr per molecule = 6

Increase in oxidation number of Fe per molecule = 1

Hence, multiplying eq. (ii) by 3 and adding in eq. (i),

$K_2Cr_2O_7 + 6FeSO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3$

To balance potassium ions and sulphate ions 1 molecule of K_2SO_4 is added to R.H.S. and 7 molecules of H_2SO_4 are added to L.H.S.

$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4$

To balance hydrogen and oxygen, $7H_2O$ should be added on R.H.S. Hence, the balanced equation is

$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$

29.

	$Al(OH)_3$ $\rightleftharpoons$	Al^{3+}	+ $3OH^-$
Conc. at $t = 0$	1	0	0
Conc. at equilibrium	$1 - S$	S	$3S$

$K_{sp} = [Al^{3+}][OH^-]^3 = (S)(3S)^3 = 27S^4$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7\times10^{-11}}{27} = 1\times10^{-12}$$

$S = 1 \times 10^{-3}$ mol L^{-1}

Molar mass of $Al(OH)_3$ = 78 g

$\therefore$ Solubility of $Al(OH)_3$ in g $L^{-1} = 1 \times 10^{-3} \times 78$
$= 78 \times 10^{-3} = 7.8 \times 10^{-2}$ g L^{-1}

pH of the solution : $S = 1 \times 10^{-3}$ mol L^{-1}

$[OH^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$

pOH = $-\log[OH^-] = -\log(3 \times 10^{-3})$

pOH = 3 – log 3 = 3 – 0.4771 = 2.523

pH = 14 – pOH = 14 – 2.523 = 11.47

OR

(i) For the reverse reaction : $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

$$K_c' = \frac{1}{K_c} = \frac{1}{8.3\times10^{-3}} = 120.48$$

(ii) (a) The value of equilibrium constant is constant for a particular reaction at a particular temperature hence, increase in pressure will have no effect.

(b) As the reaction is endothermic, the increase in temperature will favour the forward reaction. More PCl_5 will dissociate to form PCl_3 and Cl_2 hence, K_c will increase.

30. (i) We cannot place $CuSO_4$ solution in a zinc vessel, because Zn ($E°$ = –0.76 V) is stronger reducing agent than Cu($E°$ = +0.34 V). So, Zn can displace Cu from its salt solution.

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) We can store $CuSO_4$ solution in a silver vessel, because Ag ($E°$ = +0.80 V) is stronger oxidising agent than Cu ($E°$ = +0.34 V). So, Ag cannot displace Cu from its salt solution.

(iii) We can store $CuSO_4$ solution in a gold vessel, because Au ($E°$ = +1.40 V) is stronger oxidising agent than Cu ($E°$ = +0.34 V). So, Au cannot displace Cu from its salt solution.

31. When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half *i.e.*, 0.001 M.

$$\underset{0.001\text{ M}}{NaIO_3} \longrightarrow \underset{0.001\text{ M}}{Na^+} + IO_3^-$$

$$\underset{0.001\text{ M}}{Cu(ClO_3)_2} \longrightarrow \underset{0.001\text{ M}}{Cu^{2+}} + 2ClO_3^-$$

$\therefore$ After mixing, $[IO_3^-] = [NaIO_3] = 0.001$ M

$[Cu^{2+}] = [Cu(IO_3)_2] = 0.001$ M

Solubility equilibrium for copper iodate may be written as,

$$Cu(IO_3)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2IO^-_{3(aq)}$$

Ionic product of copper iodate

$= [Cu^{2+}][IO_3^-]^2 = (0.001)(0.001)^2 = 1 \times 10^{-9}$

Since ionic product (1×10^{-9}) is less than $K_{sp}(7.4 \times 10^{-8})$, therefore, no precipitation will take place.

32. If we use the relation, pH = – log $[H_3O^+]$, we get pH equal to 8. But this is not correct because an acidic solution cannot have pH greater than 7. It may be noted that in very dilute acidic solutions, when H^+ concentration from acid and water are comparable, the concentration of H^+ from water cannot be neglected. Therefore,

$[H^+]_{Total} = [H^+]_{acid} + [H^+]_{water}$

Since HCl is strong acid and is completely ionised

$[H^+]_{HCl} = 1.0 \times 10^{-8}$ M

The concentration of H^+ from ionisation of water is equal to the $[OH^-]$ from water,

$[H^+]_{H_2O} = [OH^-]_{H_2O} = x$ M (Let)

$[H^+]_{total} = (1.0 \times 10^{-8} + x)$ M

But $[H^+][OH^-] = 1.0 \times 10^{-14}$

$\therefore$ $(1.0 \times 10^{-8} + x)(x) = 1.0 \times 10^{-14}$

$\Rightarrow$ $x^2 + 10^{-8}x - 10^{-14} = 0$

On solving for x, we get $x = 9.5 \times 10^{-8}$

$\therefore$ $[H^+] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8}$
$= 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$

pH = – log $[H^+]$ = – log (1.05×10^{-7}) = 6.98

OR

(a) $[H^+] = 3.8 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(3.8 \times 10^{-3})$

$= 3\log 10 - \log 3.8 = 3 - 0.5797$

$pH = 2.4203 \approx 2.42$

(b) When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

33. The balanced redox reactions involving oxidation of Fe^{2+} ions by $Cr_2O_7^{2-}$ and MnO_4^- respectively are :

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Suppose V_2 cm^3 of M_2 M Fe^{2+} is titrated against 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ and V_1 cm^3 of 0.1 M MnO_4^- solutions, then,

$$\frac{24.5 \times 0.1}{1}(Cr_2O_7^{2-}) = \frac{M_2V_2}{6}(Fe^{2+}) \quad \text{...(i)}$$

and $$\frac{V_1 \times 0.1}{1}(MnO_4^-) = \frac{M_2V_2}{5}(Fe^{2+}) \quad \text{...(ii)}$$

Equating (i) and (ii), $V_1 = 24.5 \times \frac{6}{5} = 29.4$ cm^3

34. Since $E°$ of Cu^{2+}/Cu electrode (+ 0.34 V) is higher than that of H^+/H_2 electrode (0.0 V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and hence Cu dissolved in dil. HCl. In contrast, the electrode potential of NO_3^- ion, *i.e.*, NO_3^- /NO electrode (+ 0.97 V) is higher than that of copper electrode and hence it can oxidise Cu to Cu^{2+} ions and hence Cu dissolves in dil. HNO_3. Thus, Cu dissolves in dil. HNO_3 due to oxidation of Cu by NO_3^- ions and not by H^+ ions.

35. (i) The potential difference between two electrodes can be determined by connecting them to a voltmeter. Therefore, it is not possible to determine the potential of a single electrode because a single electrode constitutes a half-cell and a half-cell reaction cannot take place independently.

An electrode in a half cell cannot lose or gain electrons by itself. For transfer of electrons, one half cell has to be connected to some other half cell. Thus, we cannot determine the absolute value of electrode potential of a single electrode. In other words, only relative value of electrode potential can be determined by connecting the half cell with some standard electrode as the reference electrode.

(ii) The electrode potential of iron, (*i.e.*, $E°_{Fe^{2+}/Fe} = -0{\cdot}44$ V) is lower than that of copper (*i.e.*, $E°_{Cu^{2+}/Cu} = +0{\cdot}34$ V) and hence Fe has greater tendency to get converted into Fe^{2+} ions than Cu. In other words, iron undergoes oxidation more readily than copper.

(iii) An electrode with lower electrode potential has more tendency to get oxidised. In other words, it has more tendency to release electrons, and hence acts as a reducing agent.

(iv) Copper ($E°_{Cu^{2+}/Cu} = +\,0{\cdot}34$ V) has lower electrode potential than silver ($E°_{Ag^+/Ag} = +0.80$ V). Therefore, Cu releases electrons and gets oxidised to Cu^{2+} ions while Ag^+ ions accept these electrons and get reduced to Ag metal.

$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

The chemical energy of this reaction appears as heat and hence the solution becomes hot. Since, the reverse reaction cannot occur (because the $E°$ of Ag is higher than that of Cu). Therefore, no change is observed.

(v) Fe has lower electrode potential ($E°_{Fe^{2+}/Fe} = -\,0{\cdot}44$ V) than that of hydrogen ($E°_{H^+/H_2} = 0{\cdot}0$ V), therefore, Fe is a better reducing agent than H_2 and hence reduces H^+ ions to produce H_2 gas.

$$Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$$

In contrast, Ag has higher electrode potential ($E°_{Ag^+/Ag} = +\,0.80$ V) than hydrogen. Therefore, H_2 is a better reducing agent than Ag. In other words, Ag cannot reduce H^+ ions to produce H_2 gas.

OR

(i) $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$(oxidation) ;

$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$ (reduction)

Zn is oxidised to $Zn^{2+}_{(aq)}$, Pb^{2+} is reduced to Pb ;

Pb^{2+} is the oxidiser and Zn is the reducer.

(ii) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ (reduction);

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

Fe^{3+} is reduced to Fe^{2+}, I^- is oxidised to I_2;

I^- is the reducer and Fe^{3+} is the oxidiser.

(iii) $2Na \longrightarrow 2Na^+ + 2e^-$ (oxidation);

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ (reduction)

Na is oxidised to Na^+ and Cl_2 is reduced to Cl^-;

Na is the reducer and Cl_2 is the oxidiser.

(iv) $Mg \longrightarrow Mg^{2+} + 2e^-$(oxidation);

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ (reduction)

Mg is oxidised to Mg^{2+} while Cl_2 is reduced to Cl^-;

Mg is the reducer and Cl_2 is the oxidiser.

(v) $Zn \longrightarrow Zn^{2+} + 2e^-$ (oxidation);

$2H^+ + 2e^- \longrightarrow H_2$(reduction)

Zn is oxidised to Zn^{2+} while H^+ is reduced to H_2;

Zn is the reducer and H^+ is the oxidiser.

36. (i) (a) From the graph, it is clear that in 1 to 5 h,

$\Delta[A] = (0.3 - 0.5)$ mol L^{-1} = -0.2 mol L^{-1}

$\Delta[B] = (0.6 - 0.2)$ mol L^{-1} = 0.4 mol L^{-1}

The amount of B formed is double the amount of A consumed. So, in the equation, $A \rightleftharpoons nB$,
At equilibrium, n is 2.

(b) $[A]_{eq} = 0.3\text{ mol L}^{-1}$; $[B]_{eq} = 0.6\text{ mol L}^{-1}$

$$K_{eq} = \frac{[B]^2}{[A]} = \frac{(0.6\text{ mol L}^{-1})^2}{0.3\text{ mol L}^{-1}} = 1.2\text{ mol L}^{-1}$$

(ii) (a) Liquid NH_3 undergoes self ionisation according to the reaction, $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

Thus, in liquid ammonia the strongest acid is NH_4^+ and the strongest base is NH_2^-.

Thus, all ammonium salts act as acids and amides act as bases in liquid NH_3.

(b) $CO_{2(g)} + nH_2O_{(l)} \rightleftharpoons CO_{2(aq)}$

The process occurs with decrease in randomness. Since this reaction is feasible, it must be exothermic in the forward direction. Therefore, the increase of temperature pushes the reaction in the backward direction, thereby decreasing the solubility.

OR

(i) 1.5 M Na_2CO_3 gives $[CO_3^{2-}] = 1.5$ M

K_{sp} for $Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}]$

$$\therefore\quad [Ag^+] = \sqrt{\frac{K_{sp}\text{ for }Ag_2CO_3}{[CO_3^{2-}]}} = \sqrt{\frac{8.2\times10^{-12}}{1.5}}$$

$= 2.34 \times 10^{-6}$ M

K_{sp} for AgCl $= [Ag^+]\,[Cl^-]$

$$= (2.34 \times 10^{-6})\left(\frac{0.0026}{35.5}\right) = 1.71 \times 10^{-10}$$

(ii) $Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

$\therefore\quad K_{sp} = [Pb^{2+}][OH^-]^2 = s \times (2s)^2 = 4s^3$

$= 4 \times (6.7 \times 10^{-6})^3 = 1.20 \times 10^{-15}$

In a solution with pH = 8, $[H^+] = 10^{-8}$ and $[OH]^- = 10^{-6}$

$\therefore\quad 1.20 \times 10^{-15} = [Pb^{2+}] \times (10^{-6})^2$

$$\text{or}\quad [Pb^{2+}] = \frac{1.20\times10^{-15}}{(10^{-6})^2} = 1.20 \times 10^{-3}\text{ M}$$

37. (i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$\Delta n = 2 - 4 = -2$; ($T = 400 + 273$ K = 673 K)

$K_p = K_c\,(RT)^{\Delta n}$

$1.64 \times 10^{-4}\text{ atm}^{-2} = K_c\,(0.0821\text{ L atm K}^{-1}\text{ mol}^{-1} \times 673\text{ K})^{-2}$

$$\text{or}\quad K_c = \frac{1.64\times10^{-4}\text{atm}^{-2}}{(0.0821\times673\text{ L atm mol}^{-1})^{-2}} = 0.5006\text{ L}^2\text{mol}^{-2}$$

Now, $\Delta G° = -2.303\,RT\log K$

If $K = K_p$, $\Delta G° = -2.303 \times (8.314\text{ JK}^{-1}\text{ mol}^{-1})\,(673\text{ K}) \times \log(1.64 \times 10^{-4})$

$= -2.303 \times 8.314 \times 673 \times (-3.7852)\text{ J mol}^{-1}$

$= +48.78\text{ kJ mol}^{-1}$

If $K = K_c$,

$\Delta G° = -2.303 \times (8.314\text{ JK}^{-1}\text{ mol}^{-1})\,(673\text{ K}) \times \log(0.5006)$

$= -2.303 \times 8.314 \times 673 \times (-0.3005)\text{ J mol}^{-1}$

$= 3.87\text{ kJ mol}^{-1}$

(ii) From the relation $K_p = K_c\,(RT)^{\Delta n_g}$, if $\Delta n_g = 0$, $K_p = K_c$

e.g., $H_2 + I_2 \rightleftharpoons 2HI$

$\Delta n_g = (2 - 2) = 0$

OR

(i) Pyridine is a weak base. Thus, pyridine + pyridinium chloride solution is a basic buffer. Hence,

pOH = pK_b + log [Salt]/[Base]

$\because\quad pK_b = -\log K_b = -\log(1.5 \times 10^{-9})$

$= 9 - 0.1761 = 8.8239$

[Pyridine] = 0.20 M (Given),

$$[\text{Pyridinium chloride}] = \frac{0.15}{500} \times 1000 = 0.30\text{ M}$$

$$\therefore\quad \text{pOH} = 8.8239 + \log\frac{0.30}{0.20} = 8.8239 + 0.1761 = 8.999$$

i.e., $-\log[OH^-] = 8.999 \Rightarrow [OH^-] = 1.002 \times 10^{-9}$

$[OH^-]$ from $H_2O = 10^{-7}$ M cannot be neglected.

Hence, total $[OH^-] = 1.002 \times 10^{-9} + 10^{-7}$

$= 10^{-9}(1.002 + 100) = 101.002 \times 10^{-9}\text{ M} \approx 1.01 \times 10^{-7}$ M

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.01\times10^{-7}} = 9.9 \times 10^{-8}\text{ M}$$

pH $= -\log[H^+] = -\log(9.9\times 10^{-8}) = 8 - 0.9956 = 7.009$

(ii) On the basis of Le Chatelier's principle in each case,

(a) Equilibrium will shift in the forward direction.

(b) Equilibrium will shift in the backward direction.

(c) Equilibrium will shift in the backward direction.

(d) Equilibrium will shift in the forward direction

MONTHLY TEST DRIVE

XI

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks : 120

Hydrogen/The *s*-Block Elements

Time Taken : 60 Min.

NEET / AIIMS

Only One Option Correct Type

1. One mole of magnesium nitride on reacting with an excess of water gives
(a) one mole of ammonia
(b) two moles of nitric acid
(c) two moles of ammonia
(d) one mole of nitric acid.

2. The bond angle and dipole moment of water respectively are
(a) 109.5°, 1.84 D (b) 104.5°, 1.56 D
(c) 104.5°, 1.84 D (d) 102.5°, 1.56 D

3. An unknown inorganic compound (*X*) loses its water of crystallisation on heating and its aqueous solution gives the following reactions.
(I) It gives a white turbidity with dilute HCl solution.
(II) It decolourises a solution of iodine in potassium iodide.
(III) It gives a white precipitate with silver nitrate solution which turns black on standing.
The compound (*X*) is
(a) $Na_2CO_3\cdot 10H_2O$ (b) $Na_2S_2O_3\cdot 5H_2O$
(c) $Na_2SO_4\cdot 10H_2O$ (d) none of these.

4. The solubility of lithium halides in non-polar solvents follows the order
(a) LiI > LiBr > LiCl > LiF
(b) LiF > LiI > LiBr > LiCl
(c) LiCl > LiF > LiI > LiBr
(d) LiBr > LiCl > LiF > LiI

5. Some statements about heavy water are given below:
(i) Heavy water is used as a moderator in nuclear reactors.
(ii) Heavy water is more associated than ordinary water.
(iii) Heavy water is more effective solvent than ordinary water.
Which of the above statements are correct?
(a) (i) and (ii) (b) (i), (ii) and (iii)
(c) (ii) and (iii) (d) (i) and (iii)

6. Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}
(a) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

7. $BaSO_4$ is water insoluble although it is an ionic compound because of
(a) low lattice energy
(b) high bond energy
(c) lattice energy > solvation energy
(d) solvation energy > lattice energy.

8. A metal *M* readily forms its sulphate MSO_4 which is water-soluble. It forms its oxide *M*O which becomes inert on heating. It forms an insoluble hydroxide $M(OH)_2$ which is soluble in NaOH solution. Then *M* is
(a) Mg (b) Ba
(c) Ca (d) Be

9. The electron affinity of Be is similar to
(a) He (b) B (c) Li (d) Na

10. Monovalent sodium and potassium ions, divalent magnesium and calcium ions are found in
(a) lipids (b) biological fluids
(c) fats (d) enzymes.

11. $NH_4Cl + (A) \longrightarrow$ Microcosmic salt $\xrightarrow{\text{Heat}} (B) \xrightarrow[+\,MnO]{\text{Heat}} (C)$ Violet bead

(A), (B) and (C) are

(a) Na_3PO_4, $NaPO_3$, $Mn_3(PO_4)_2$
(b) Na_2HPO_4, Na_3PO_4, $Mn_3(PO_4)_2$
(c) Na_2HPO_4, $NaPO_3$, $Mn(PO_3)_2$
(d) Na_2HPO_4, $NaPO_3$, $NaMnPO_4$

12. Oxidation state of hydrogen is zero in
(a) CaH_2 (b) NaH
(c) PdH_2 (d) NH_3

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** H_2O_2 is stored in wax-lined glass or plastic vessels.
Reason : H_2O_2 decomposes slowly on exposure to light.

14. **Assertion :** Sulphides are oxidised by H_2O_2 in presence of Fe (III).
Reason : Fe (III) reduces sulphide to sulphate.

15. **Assertion :** Li_2CO_3 decomposes easily on heating to form Li_2O and CO_2.
Reason : Li^+ is very small in size and applies very high polarising power on CO_3^{2-} ion leading to the decomposition of Li_2CO_3.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. Read the following statements.
I. Cs^+ is highly hydrated.
II. Li has highest melting point among Li, Na, K and Rb.
III. In alkali metals, only Li forms nitride.
The correct statements are
(a) I and II (b) II and III
(c) I and III (d) I, II and III

17. The melting point of most of the solid substances increase with an increases of pressure. However, ice melts at a temperature lower than its usual melting point when pressure is increased. This is because
(a) ice is less denser than H_2O
(b) pressure generates heat
(c) the chemical bonds break under pressure
(d) ice is not a true solid.

18. Decomposition of H_2O_2 is retarded by
(a) H_3PO_4 (b) alcohol
(c) acetanilide (d) all of these.

19. Identify the correct statement.
(a) The percentage of calcium is lower in gypsum in comparison to plaster of Paris.
(b) Gypsum is not a natural product. It is obtained by heating of plaster of Paris.
(c) Plaster of Paris is obtained by hydration of gypsum.
(d) Plaster of Paris is formed by oxidation of gypsum.

More than One Options Correct Type

20. Select the correct statements about barium.
(a) It shows photoelectric effect.
(b) It is silvery white metal.
(c) It forms $Ba(NO_3)_2$ which is used in preparation of green fire.
(d) Its ionisation energy is less than radium.

21. Highly pure dilute solution of sodium in liquid ammonia
(a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amide
(d) produces hydrogen gas.

COMIC CAPSULE

22. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with
(a) H^+ ions (b) Ca^{2+} ions
(c) SO_4^{2-} ions (d) Mg^{2+} ions.

23. Select the correct statement(s) about limelight.
(a) It is produced in oxyhydrogen flame.
(b) It is used in welding.
(c) Temperature of limelight is sufficient to melt even platinum.
(d) It is produced in an endothermic reaction.

Numerical Value Type

24. To 8.4 mL H_2O_2, excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N $Na_2S_2O_3$ solution. Volume strength of H_2O_2 solution is

25. Number of moles of acidified potassium permanganate reduced by five moles of H_2O_2 is

26. Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as 'sorel cement'. The composition of sorel cement is $MgCl_2 \cdot nMgO \cdot xH_2O$. The value of n is

Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage :
The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Some important compounds of calcium and sodium includes calcium oxide (lime), calcium sulphate (Plaster of Paris), calcium carbonate (limestone) sodium hydroxide (Caustic soda) and sodium hydrogen carbonate (Baking soda).

	Column-I (Compound)		Column-II (Use)
P.	$CaCO_3$	I	Used in gun powder
Q.	$Na_2S_2O_3 \cdot 5H_2O$	II	Used in fire extinguishers
R.	$NaNO_3$	III	Used as a flux in metallurgy
S.	$NaHCO_3$	IV	Used in black and white photography

27. Which of the following has the correct combination considering column I and column II?
(a) Q $\rightarrow$ IV (b) R $\rightarrow$ II
(c) P $\rightarrow$ I (d) S $\rightarrow$ III

28. Which of the following has the correct combination considering column I and column II?
(a) P $\rightarrow$ IV (b) Q $\rightarrow$ I
(c) R $\rightarrow$ III (d) S $\rightarrow$ II

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage :
Dihydrogen under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If 'E' is the symbol of an element then hydride can be expressed as EH_x (*e.g.*, MgH_2) or E_mH_n (*e.g.*, B_2H_6).

	Column-I (Hydride)		Column-II (Type of hydride)
P.	BeH_2	I	Complex
Q.	SiH_4	II	Interstitial
R.	LaH_3	III	Covalent
S.	$LiAlH_4$	IV	Polymeric

29. Which of the following has the correct combination considering column I and column II?
(a) P $\rightarrow$ II (b) Q $\rightarrow$ IV
(c) R $\rightarrow$ III (d) S $\rightarrow$ I

30. Which of the following has the correct combination considering column I and column II?
(a) P $\rightarrow$ IV (b) Q $\rightarrow$ I
(c) R $\rightarrow$ III (d) S $\rightarrow$ II

Keys are published in this issue. Search now! ☺

CHECK YOUR PERFORMANCE

No. of questions attempted ......
No. of questions correct ......
Marks scored in percentage ......

If your score is

> 80%	Your preparation is going good, keep it up to get high score.
60-80%	Need more practice, try hard to score more next time.
<60%	Stress more on concepts and revise thoroughly.

GET SET GO for JEE

Class XII

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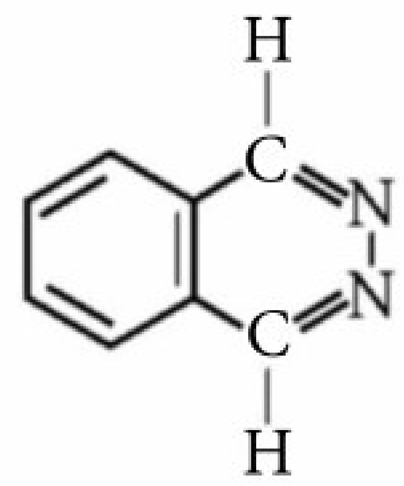
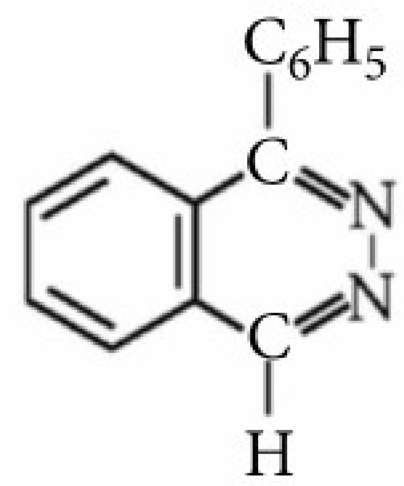
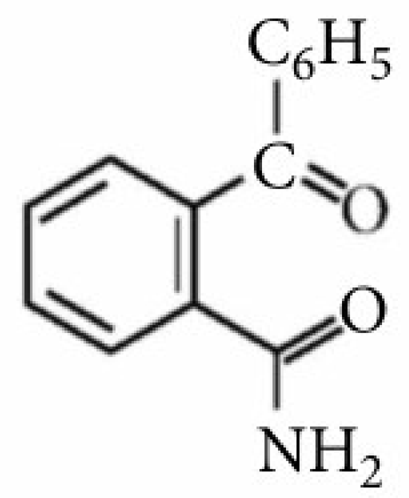
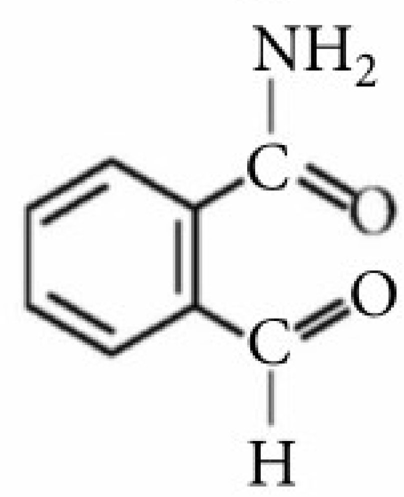
Practicing these MCQs help to strengthen your concepts and give you extra edge in your JEE preparation

Only One Option Correct Type

1. If rate constant for the first-order decomposition of ethylene oxide into CH_4 and CO follows the equation : $\log k(\text{in s}^{-1}) = 14.34 - (1.25 \times 10^4 \text{ K})/T$. Then the activation energy of the reaction, the rate constant at 700 K and frequency factor, A will be respectively
   (a) 239.3 kJ mol^{-1}, 3.02×10^{-4} s^{-1}, 2.19×10^{14} s^{-1}
   (b) 400.12 kJ mol^{-1}, 2.168×10^{-4} s^{-1}, 3.02×10^{4} s^{-1}
   (c) 339.4 kJ mol^{-1}, 2.02×10^{-10} s^{-1}, 4.50×10^{7} s^{-1}
   (d) 315.8 kJ mol^{-1}, 3.02×10^{-4} s^{-1}, 3.168×10^{14} s^{-1}.

2. A metal gives two chlorides '*A*' and '*B*'. '*A*' gives black precipitate with NH_4OH and '*B*' gives white. With KI '*B*' gives a red precipitate soluble in excess of KI. Here '*A*' and '*B*' are respectively
   (a) $HgCl_2$ and Hg_2Cl_2 (b) Hg_2Cl_2, $HgCl_2$
   (c) $HgCl_2$ and HgCl (d) none of these.

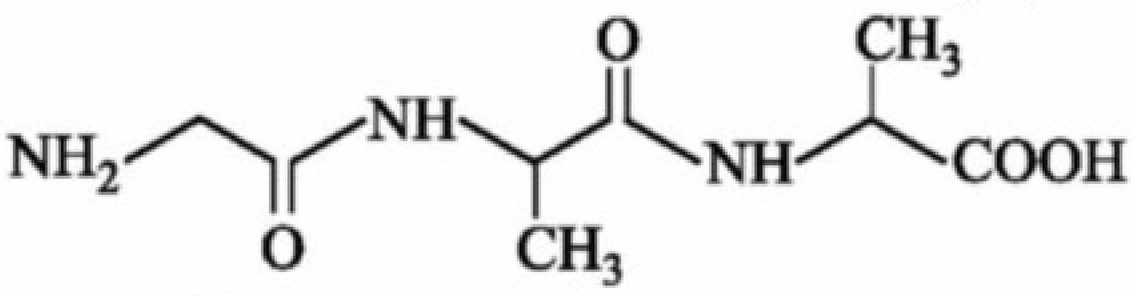
3. What will be the equilibrium constant of the cell reaction, $2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$ occurring in the zinc-silver cell at 25°C when $[Zn^{2+}] = 0.10$ M and $[Ag^+] = 10$ M? The EMF of the cell is found to be 1.62 volts.
   (a) 5.26×10^{49} (b) 6.03×10^{51}
   (c) 6.26×10^{52} (d) 8.128×10^{52}

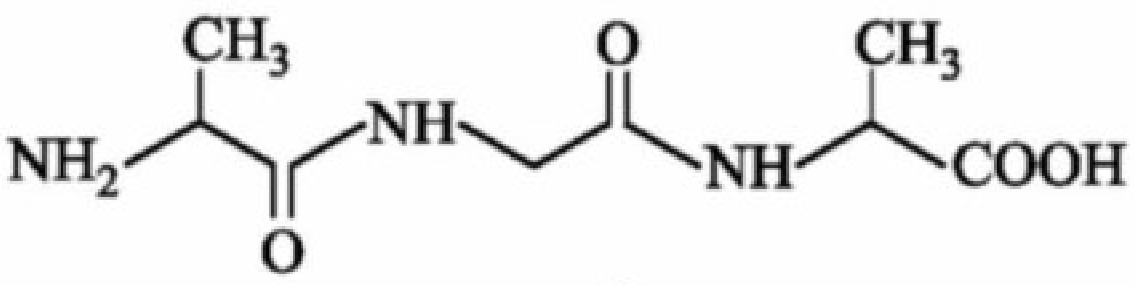
4. An organic compound A, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound B. The compound B on treatment with PCl_5, followed by reaction with H_2-Pd, $BaSO_4$ gives compound C, which on reaction with hydrazine gives a cyclised compound D. The compound D is
   (a) 
   (b) 
   (c) 
   (d) 

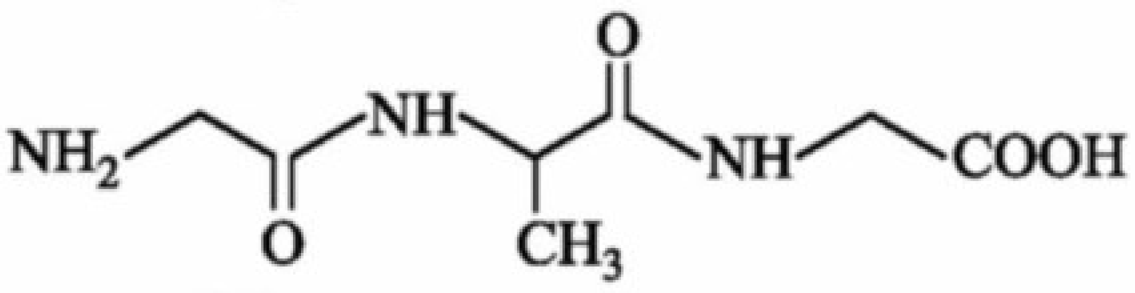
5. Ba^{2+}, CN^- and Co^{2+} form an ionic complex. If this complex is 75% ionised in aqueous solution with van't Hoff factor (i) equal to four and paramagnetic moment is equal to 1.73 B.M. (due to spin only) then, the hybridisation state of Co(II) in the complex will be
   (a) sp^3d (b) d^2sp^3 (c) sp^3d^2 (d) dsp^3

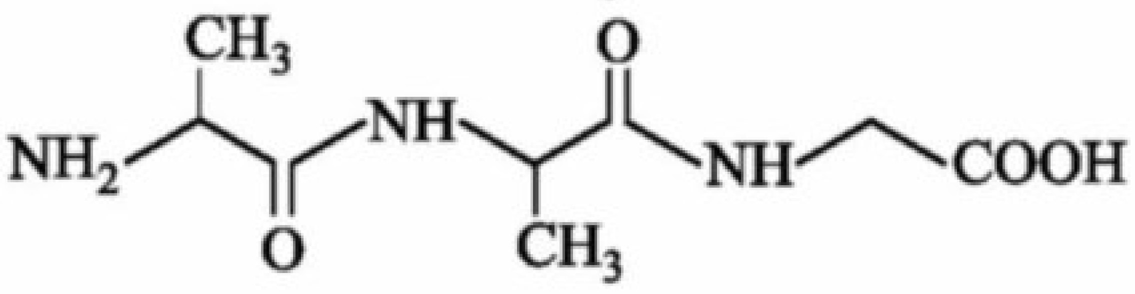
6. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
   (a) CO_2 is more volatile than CS_2.
   (b) Metal sulphides are thermodynamically more stable than CS_2.
   (c) CO_2 is thermodynamically more stable than CS_2.
   (d) Metal sulphides are less stable than the corresponding oxides.

7. A tripeptide is written as Glycine–Alanine–Glycine. The correct structure of the tripeptide is

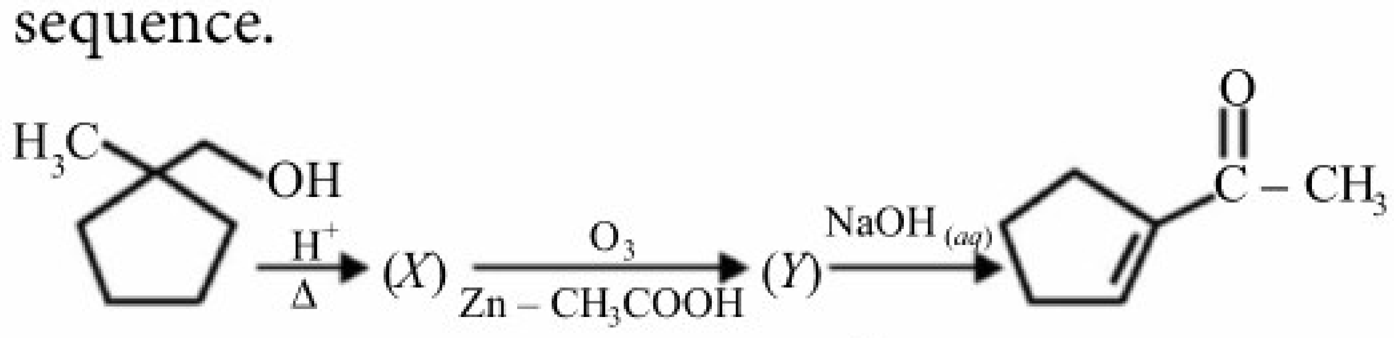
(a) 

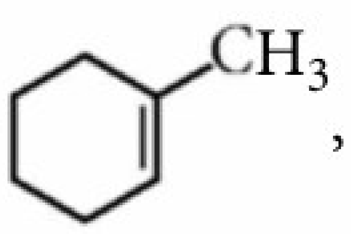
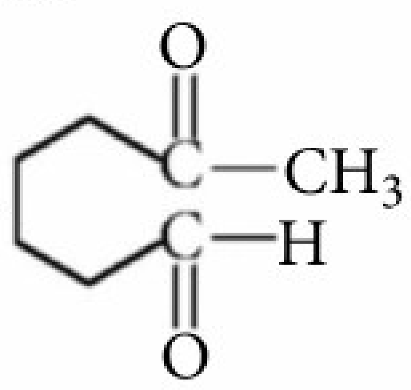
(b) 

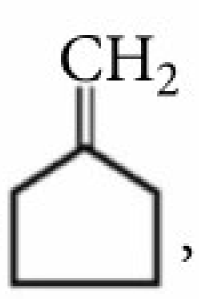
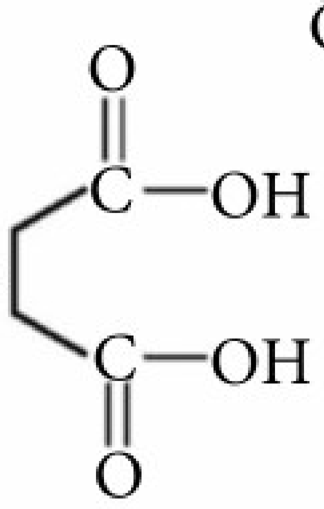
(c) 

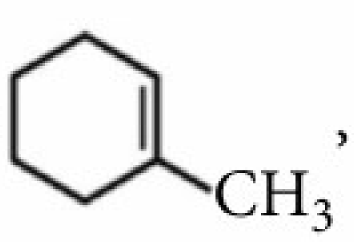
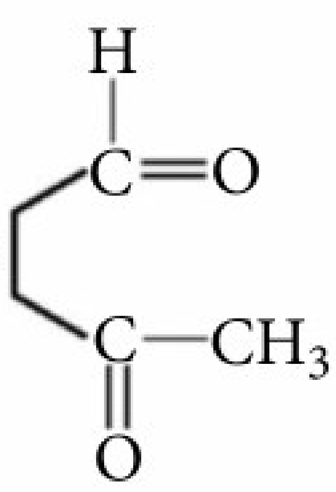
(d) 

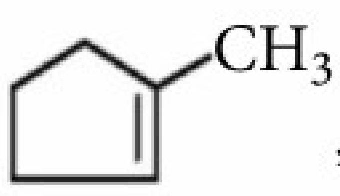
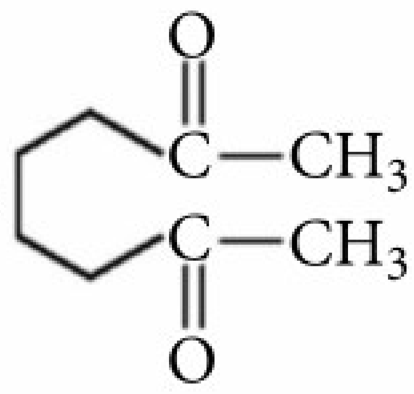
8. Identify (X) and (Y) in the following reaction sequence.



(a) $X =$  , $Y =$ 

(b) $X =$  , $Y =$ 

(c) $X =$  , $Y =$ 

(d) $X =$  , $Y =$ 

9. Which one of the following statements is not true?
   (a) Buna-S is a copolymer of butadiene and styrene.
   (b) Natural rubber is a 1,4-polymer of isoprene.
   (c) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.
   (d) Natural rubber has the *trans*-configuration at every double bond.

10. Iron (II) oxide, FeO, crystal has a cubic structure and each edge of the unit cell is 5.0 Å. If the density of the oxide is 4.0 g cm^{-3}, then what will be the number of Fe^{2+} ions present in each unit cell?
    (a) 3 (b) 2 (c) 4 (d) 6

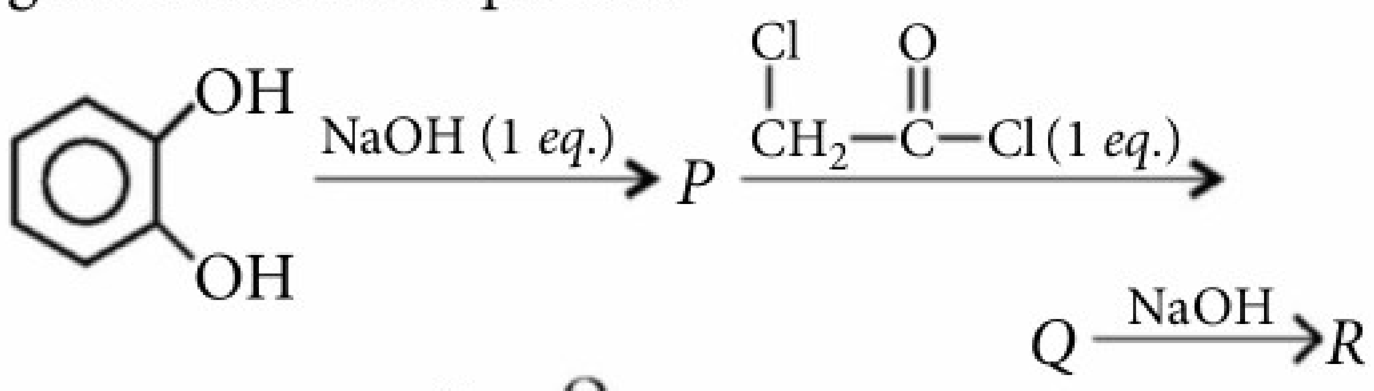
More Than One Options Correct Type

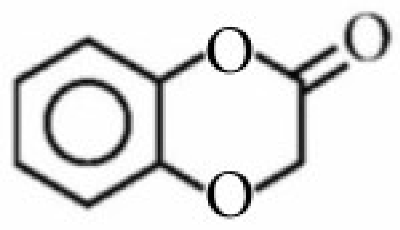
11. 1.2575 g sample of $[Cr(NH_3)_6]SO_4Cl$ (Mol. wt. = 251.5) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm at 27°C. Which of the following statements is/are correct about this solution?
    (a) Given complex furnishes three ions in solution.
    (b) The van't Hoff factor is 3.
    (c) The equilibrium molarity of $[Cr(NH_3)_6]\ SO_4Cl = 0$.
    (d) The equilibrium molarity of $[Cr(NH_3)_6]^{3+} = 0.02$ M.

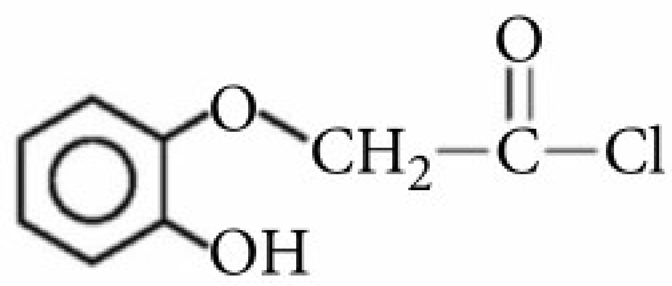
12. Nitrogen(I) oxide is produced by
    (a) thermal decomposition of ammonium nitrate
    (b) disproportionation of N_2O_4
    (c) thermal decomposition of ammonium nitrite
    (d) interaction of hydroxylamine and nitrous acid.

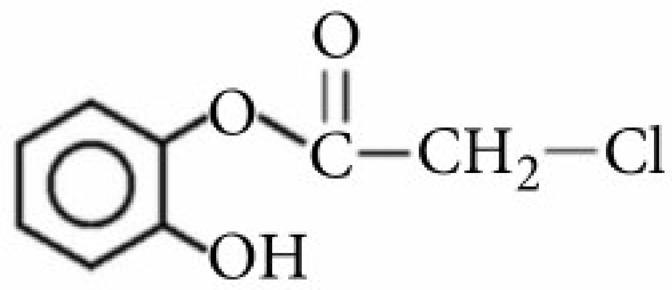
13. Which of the following is/are examples of Sandmeyer's reaction?
    (a) $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{CuCl} C_6H_5Cl$
    (b) $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{CuBr} C_6H_5Br$
    (c) $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{CuCN} C_6H_5CN$
    (d) $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow[KI]{KCN} C_6H_5I$

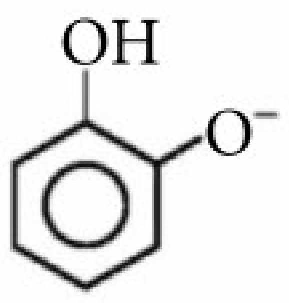
14. Which of the following is correct option for the given reaction sequence?



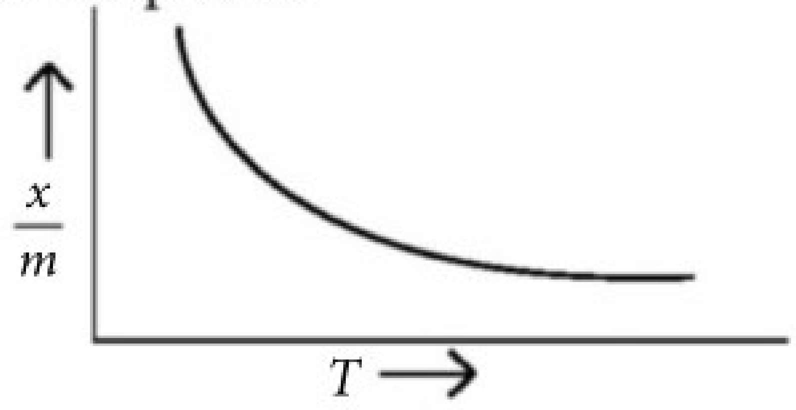
(a) $R =$ 

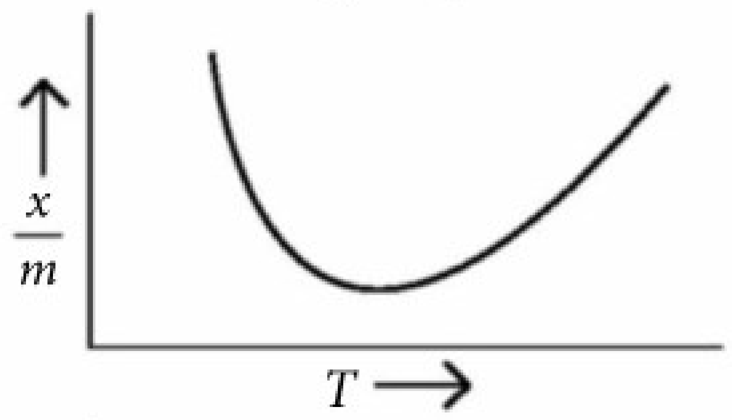
(b) $Q =$ 

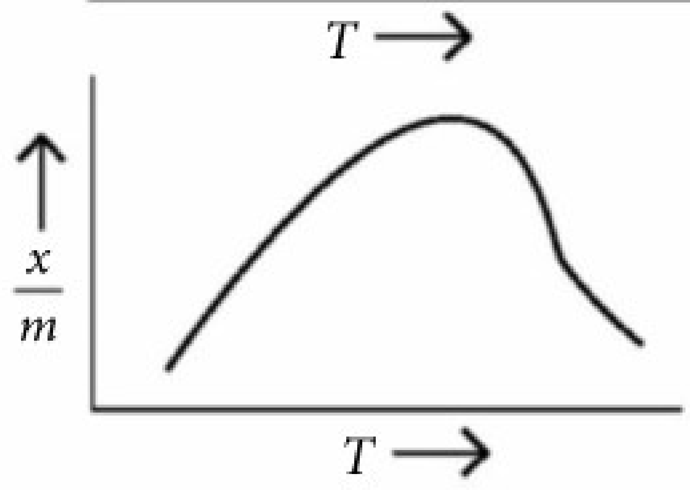
(c) $Q =$ 

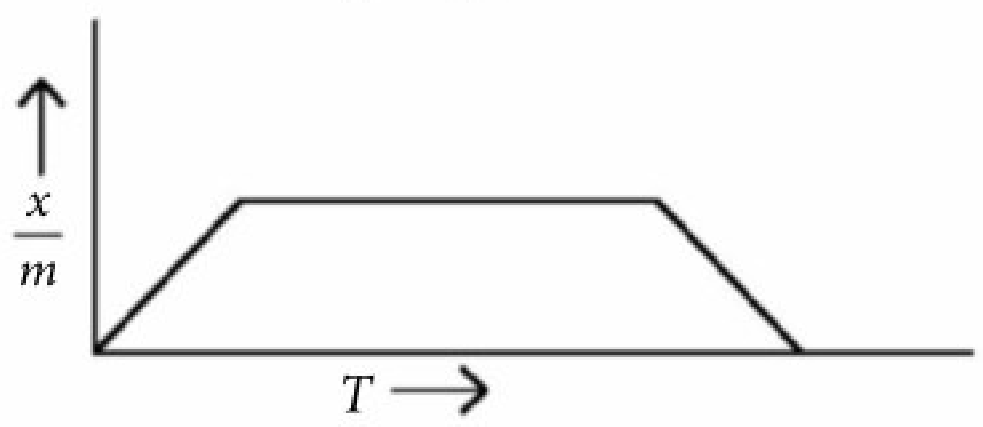
(d) $P =$ 

15. Which is not the adsorption isobar for chemisorption?

(a) 

(b) 

(c) 

(d) 

SOLUTIONS

1. **(a):** Arrhenius equation, $k = Ae^{-E_a/RT}$

or $\log k = \log A - E_a/(2.303\,RT)$ ...(i)

Also, $\log k = 14.34 - 1.25 \times 10^4\ \mathrm{K}/T$ (given) ...(ii)

Now, from eqs. (i) and (ii),

$E_a/2.303\,RT = 1.25 \times 10^4\ \mathrm{K}/T$

$\therefore$ Activation energy, $E_a = (1.25 \times 10^4\ \mathrm{K})\ (2.303)\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})$

$= 23.93 \times 10^4\ \mathrm{J\ mol^{-1}} = 239.3\ \mathrm{kJ\ mol^{-1}}$

At $T = 700$ K : $\log k = 14.34 - (1.25 \times 10^4\ \mathrm{K}/700\ \mathrm{K}) = -3.52$

$\therefore$ Rate constant, $k = 3.02 \times 10^{-4}\ \mathrm{s^{-1}}$

It is evident from Eqs. (i) and (ii) that

$\log A = 14.34$

$\therefore$ Frequency factor, $A = 2.19 \times 10^{14}\ \mathrm{s^{-1}}$

2. **(b):** 'A' is Hg_2Cl_2 and 'B' is $HgCl_2$.

$$\underset{(A)}{Hg_2Cl_2} + 2NH_4OH \longrightarrow \underbrace{Hg\begin{cases}NH_2\\Cl\end{cases} + Hg}_{\text{Black ppt.}} + NH_4Cl + 2H_2O$$

$$\underset{(B)}{HgCl_2} + 2NH_4OH \longrightarrow \underset{\text{White ppt.}}{Hg\begin{cases}NH_2\\Cl\end{cases}} + NH_4Cl + 2H_2O$$

$$\underset{(B)}{HgCl_2} + 2KI \longrightarrow \underset{\text{Red ppt.}}{HgI_2} + 2KCl$$

$$HgI_2 + \underset{\text{(Excess)}}{2KI} \longrightarrow \underset{\substack{\text{Nessler's reagent}\\\text{(Soluble)}}}{K_2HgI_4}$$

3. **(b):** For the cell,

$2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+} (n = 2)$

$$E = E° - \frac{0.0591}{n}\log K_c$$

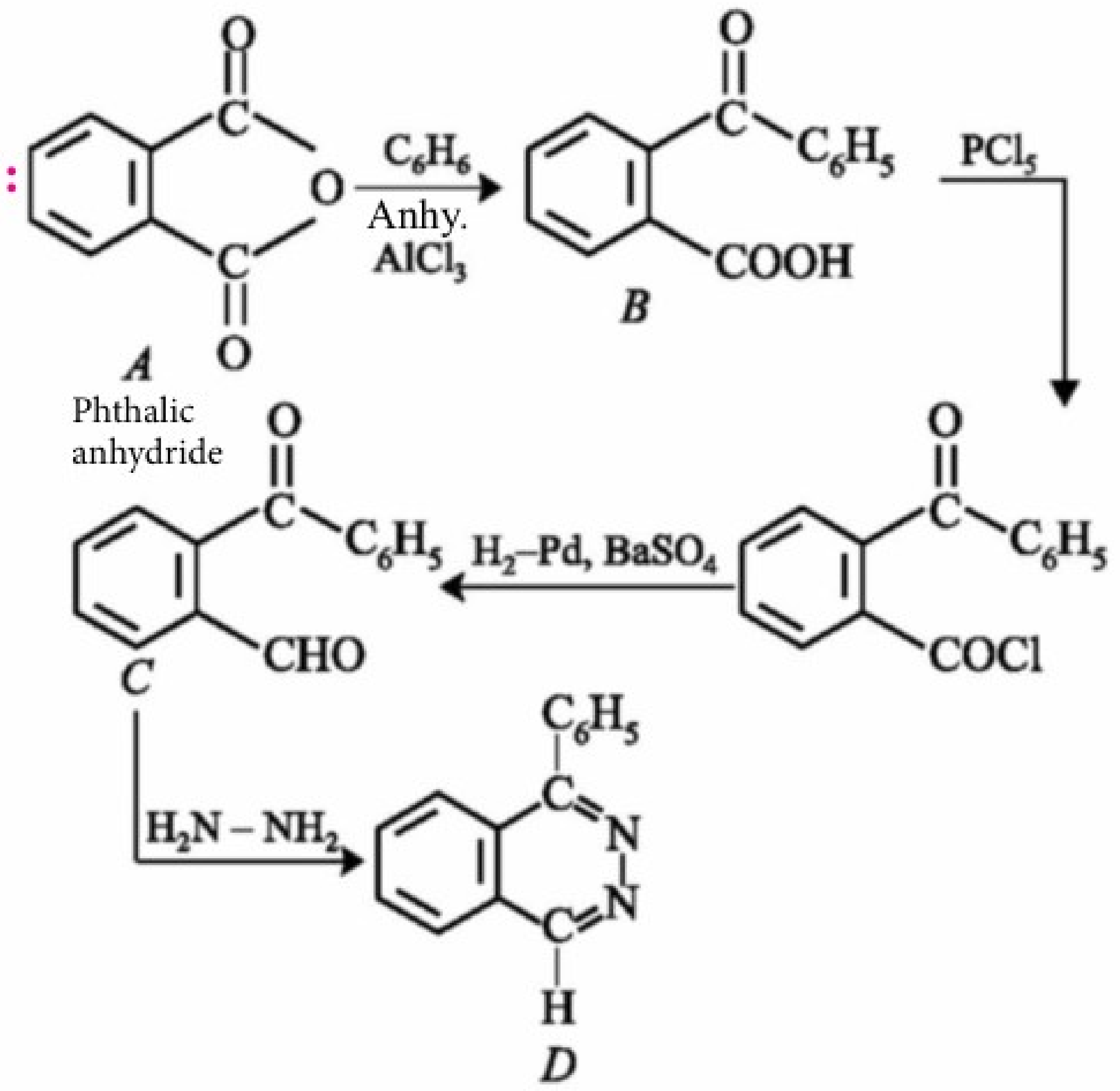
$$1.62 = E° - \frac{0.0591}{2}\log\frac{0.01}{10}$$

$E° = 1.62 - 0.089 = 1.53$ volt

$$E° = \frac{0.0591}{n}\log K_{eq} \Rightarrow 1.53 = \frac{0.0591}{2}\log K_{eq}$$

$\therefore$ $K_{eq.} = 10^{51.78} = 6.03 \times 10^{51}$

4. **(b):**

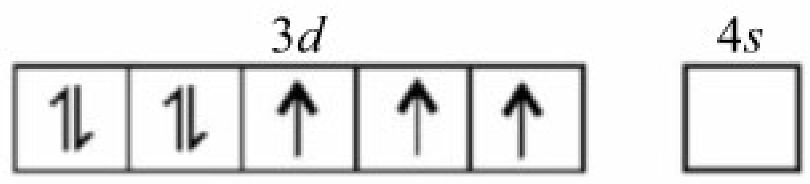


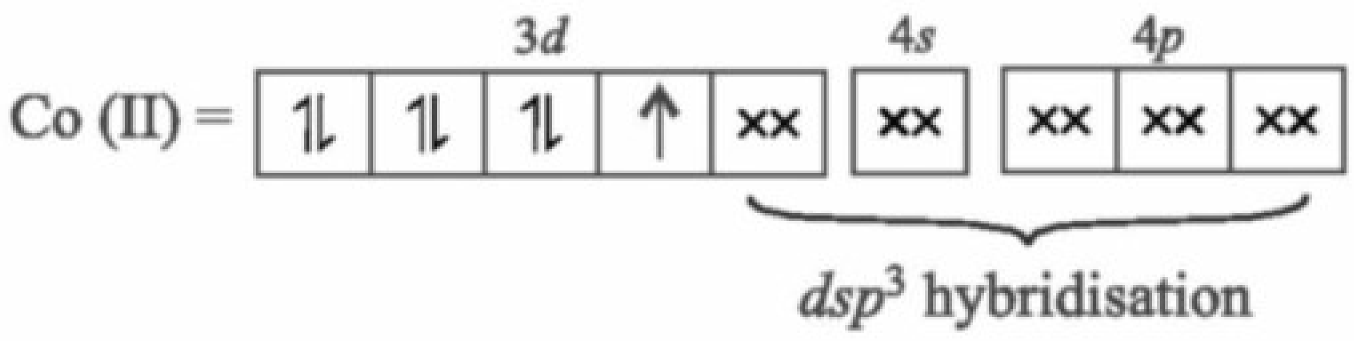
5. **(d):** As $\mu = \sqrt{n(n+2)}$ B.M.

$1.73 = \sqrt{n(n+2)}$

$\therefore \quad n = 1$

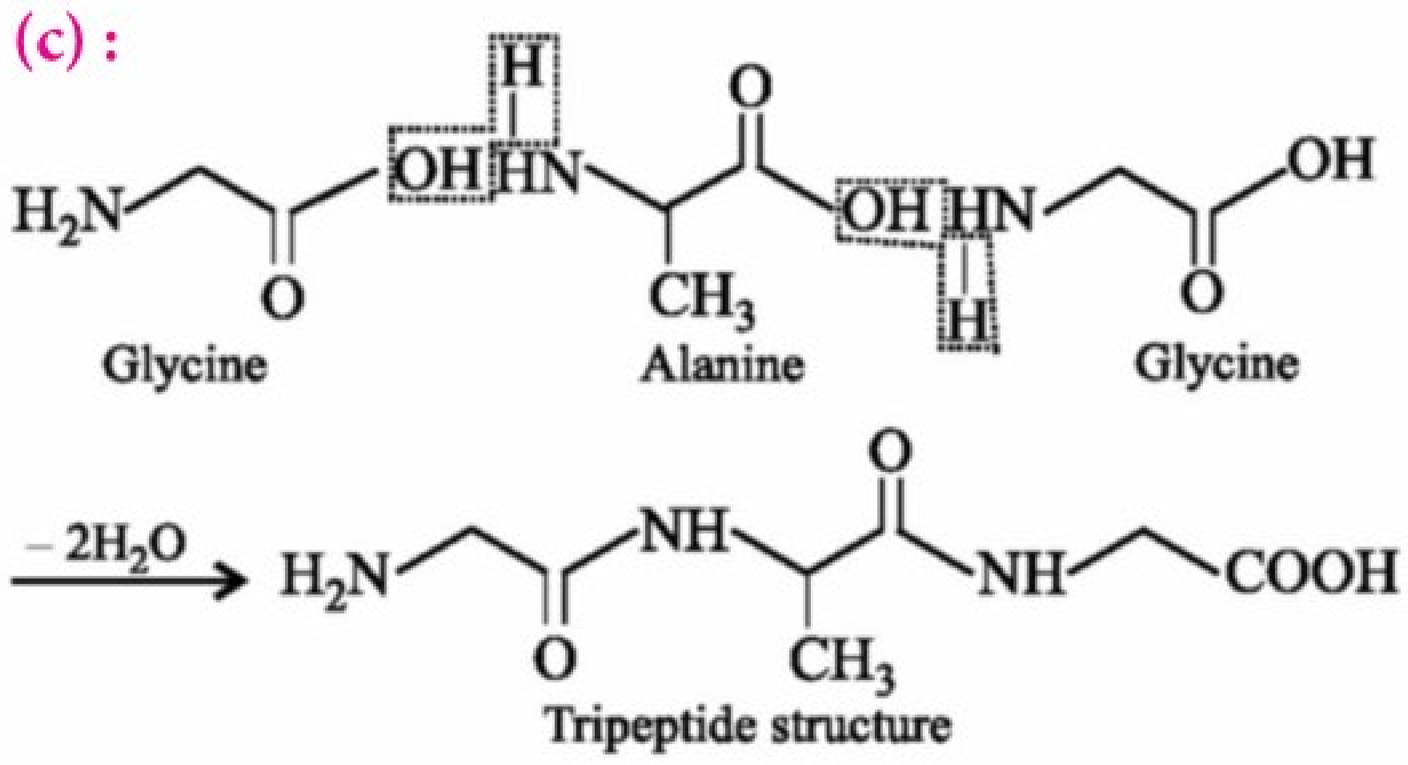
One unpaired electron indicates paramagnetic moment.

Co (II) = $3d^7\, 4s^0$ 

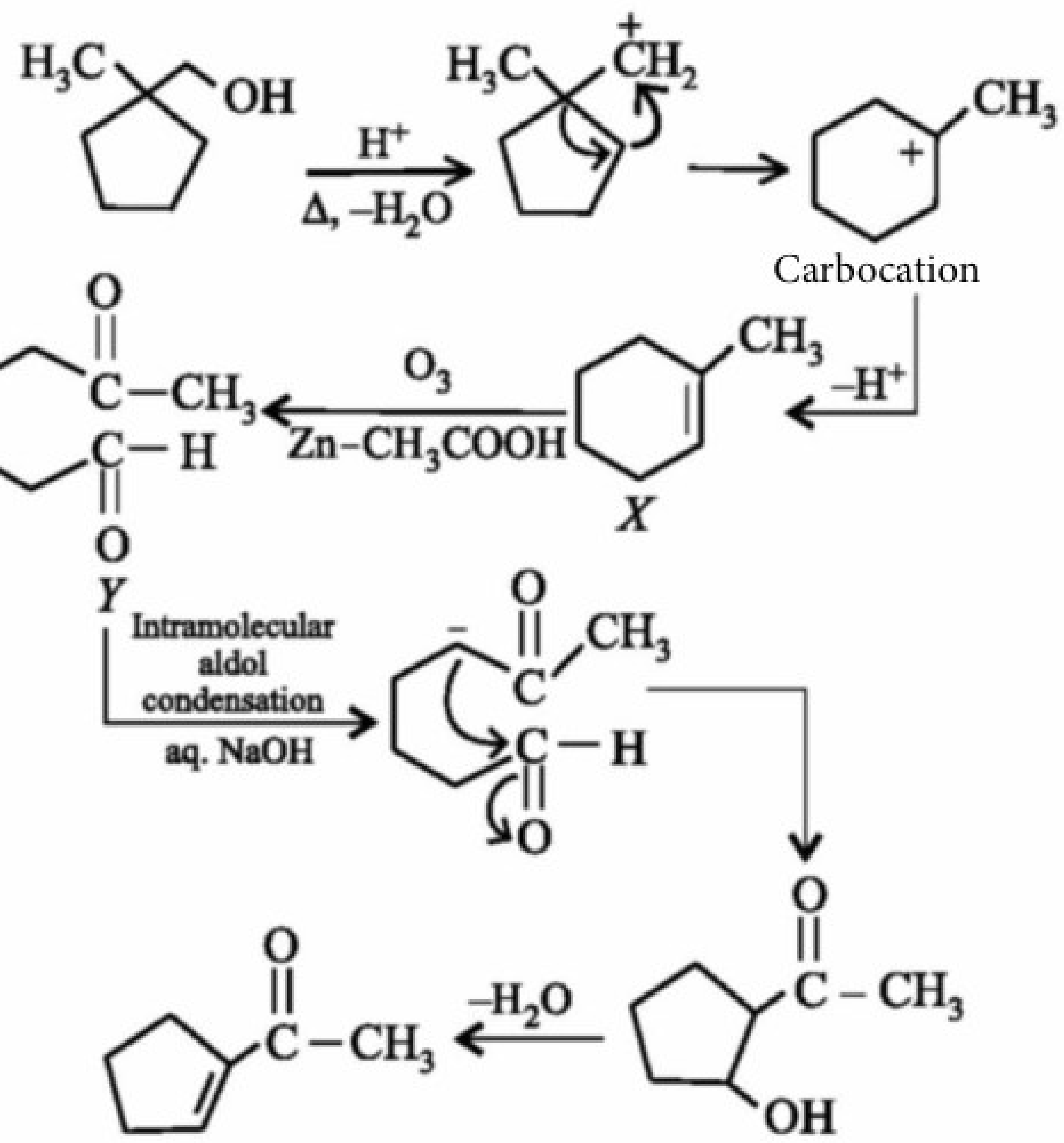


6. **(a):** The reduction process is based on the thermodynamic stability of the products and not on their volatility.

7. **(c):**



8. **(a):**



9. **(d):** Natural rubber is *cis*-1,4 polyisoprene and has only *cis*-configuration about the double bond.

10. **(c):** Volume of the unit cell = $(5 \times 10^{-8}\ \text{cm})^3$

$= 1.25 \times 10^{-22}\ \text{cm}^3$

Density of FeO = $4.0\ \text{g cm}^{-3}$

$\therefore$ Mass of the unit cell

$= 1.25 \times 10^{-22}\ \text{cm}^3 \times 4.0\ \text{g cm}^{-3} = 5.0 \times 10^{-22}\ \text{g}$

Mass of one molecule of FeO

$$= \frac{\text{Molar mass in gram}}{\text{Avogadro's number}} = \frac{72\ \text{g mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$= 1.195 \times 10^{-22}\ \text{g}$

$\therefore$ Number of FeO molecules per unit cell

$$= \frac{5.0 \times 10^{-22}\ \text{g}}{1.195 \times 10^{-22}\ \text{g}} = 4.18 \approx 4$$

Thus, there are four Fe^{2+} ions and four O^{2-} ions in each unit cell.

11. **(a, b, c, d):** Molarity $= \dfrac{w \times 1000}{M \times V_{(\text{mL})}} = \dfrac{1.2575 \times 1000}{251.5 \times 250}$

$= 0.02$ M

$\pi = CRT$

$\therefore \quad \pi_{cal} = 0.02 \times 0.0821 \times 300 = 0.4926$ atm

$$\frac{\pi_{obs}}{\pi_{cal}} = i = \frac{1.478}{0.4926} = 3$$

As the given complex is dissociated as,

$$[Cr(NH_3)_6]SO_4Cl \rightleftharpoons [Cr(NH_3)_6]^{3+} + SO_4^{2-} + Cl^-$$

	$[Cr(NH_3)_6]SO_4Cl$	$[Cr(NH_3)_6]^{3+}$	SO_4^{2-}	Cl^-
	0.02	0	0	0
Eq. conc.	0	0.02	0.02	0.02

$\therefore \quad n = 3$

$\because \quad \alpha = \dfrac{i-1}{n-1}$; $\alpha = 1$

12. **(a, d):** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$

13. **(a, b, c)** 14. **(a, c, d)**

15. **(a, b, d):** In chemisorption, adsorption first increases and then decreases with increase in temperature.

CLASS-XII

BRUSH UP for NEET/JEE 2020

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 4 The *d*- and *f*-Block Elements | Coordination Compounds

The *d*- and *f*-Block Elements

THE TRANSITION ELEMENTS (*d*-BLOCK)

- The elements that lie in between *s*-block and *p*-block elements are called transition elements as they show transitional properties between *s*- and *p*-block elements.
- *d*-Block elements in their ground state or in most common oxidation state have partially filled *d*-orbitals. General electronic configuration of *d*-block elements is $(n-1)d^{1-10}\, ns^{0-2}$.
- It is obvious from the electronic configuration that in transition elements valence electrons are present in outermost shell (*ns*) as well as in $(n-1)$ *d*-orbital *i.e.*, penultimate (last but one) shell.

Classification and Electronic Configuration of *d*-Block Elements

- **First (3*d*) Transition Series (Sc - Zn)**

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E.C.	$3d^1\,4s^2$	$3d^2\,4s^2$	$3d^3\,4s^2$	$3d^5\,4s^1$	$3d^5\,4s^2$	$3d^6\,4s^2$	$3d^7\,4s^2$	$3d^8\,4s^2$	$3d^{10}\,4s^1$	$3d^{10}\,4s^2$

- **Second (4*d*) Transition Series (Y - Cd)**

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd
E.C.	$4d^1\,5s^2$	$4d^2\,5s^2$	$4d^4\,5s^1$	$4d^5\,5s^1$	$4d^5\,5s^2$	$4d^7\,5s^1$	$4d^8\,5s^1$	$4d^{10}\,5s^0$	$4d^{10}\,5s^1$	$4d^{10}\,5s^2$

*Technetium (Tc) is a synthetic transition metal.

- **Third (5*d*) Transition Series (La- Hg)**

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
E.C.	$5d^1\,6s^2$	$5d^2\,6s^2$	$5d^3\,6s^2$	$5d^4\,6s^2$	$5d^5\,6s^2$	$5d^6\,6s^2$	$5d^7\,6s^2$	$5d^9\,6s^1$	$5d^{10}\,6s^1$	$5d^{10}\,6s^2$

- **Fourth (6*d*) Transition Series (Ac - Cn)**

At. No.	89	104	105	106	107	108	109	110	111	112
Element	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
E.C.	$6d^1\,7s^2$	$6d^2\,7s^2$	$6d^3\,7s^2$	$6d^4\,7s^2$	$6d^5\,7s^2$	$6d^6\,7s^2$	$6d^7\,7s^2$	$6d^8\,7s^2$	$6d^{10}\,7s^1$	$6d^{10}\,7s^2$

General Characteristics

Melting and boiling points	High due to strong metallic bonding.
Enthalpies of atomisation	High due to strong interatomic interactions.
Oxidation states	Variable due to participation of *ns* and $(n-1)d$ electrons.
Metallic Character	Except mercury, all transition elements have typical metallic structure and show all the properties of metals.
Complex formation	Form complexes due to high nuclear charge and small size and availability of empty *d*-orbitals to accept lone pair of electrons donated by ligands.
Coloured compounds	Mostly form coloured compounds due to *d*-*d* transitions.
Magnetic properties	Transition metal ions and their compounds are generally paramagnetic due to presence of unpaired electrons in the $(n-1)d$-orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where, *n* is the no. of unpaired electrons.
Catalytic behaviour	Due to variable oxidation states and ability to form complexes.
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated.
Alloy formation	Due to similar atomic sizes.

General Trends

Ionisation Energy	**Atomic size**	**M.Pt. and B.Pt.**	**Density**
Increases slowly due to ineffective shielding of nuclear charge by *d*-electrons which tend to attract the outer electron cloud with greater force.	Decreases slowly in the series upto the middle due to ineffective shielding of *d*-electrons and increased nuclear charge but at the end of the series there is a slight increase in atomic radii due to increased electron-electron repulsion between added electrons in the same orbital.	First increase, rise to maximum then decrease because number of unpaired electrons first increase then decrease.	Increases along a series because atomic size decreases whereas atomic mass increases.

Electrode potential ($E°$)

- $E°(M^{n+}/M)$ is governed by three factors :
  - Heat of sublimation
  - Heat of ionisation
  - Heat of hydration

  For the 3*d*-transition metals the $E°(M^{2+}/M)$ values (in volts) are :

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
–1.63	–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76

  The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper, 3*d*-elements are good reducing agents but weaker than *s*-block elements.

Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

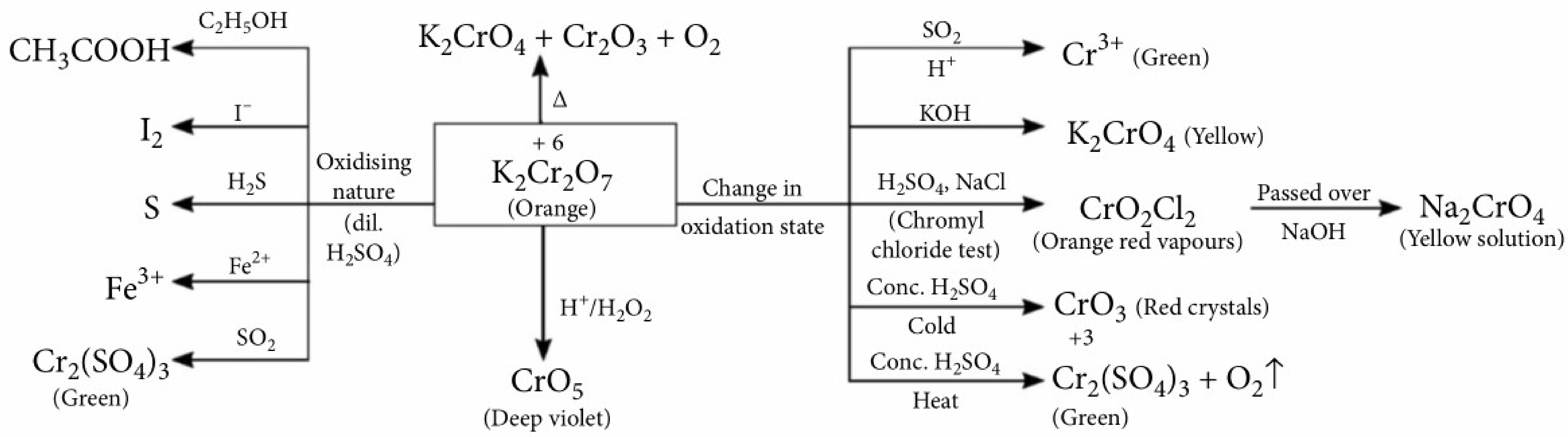
- **Preparation :** It is prepared from chromite ore or ferrochrome ($FeCr_2O_4$).

  $$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

  $$2Na_2CrO_4 + H_2SO_4\,(\text{conc.}) \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

  $$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

- **Properties :**
  - $K_2Cr_2O_7$ is soluble in hot water.
  - It is in the form of orange crystals which melt at 400 °C.



Uses :

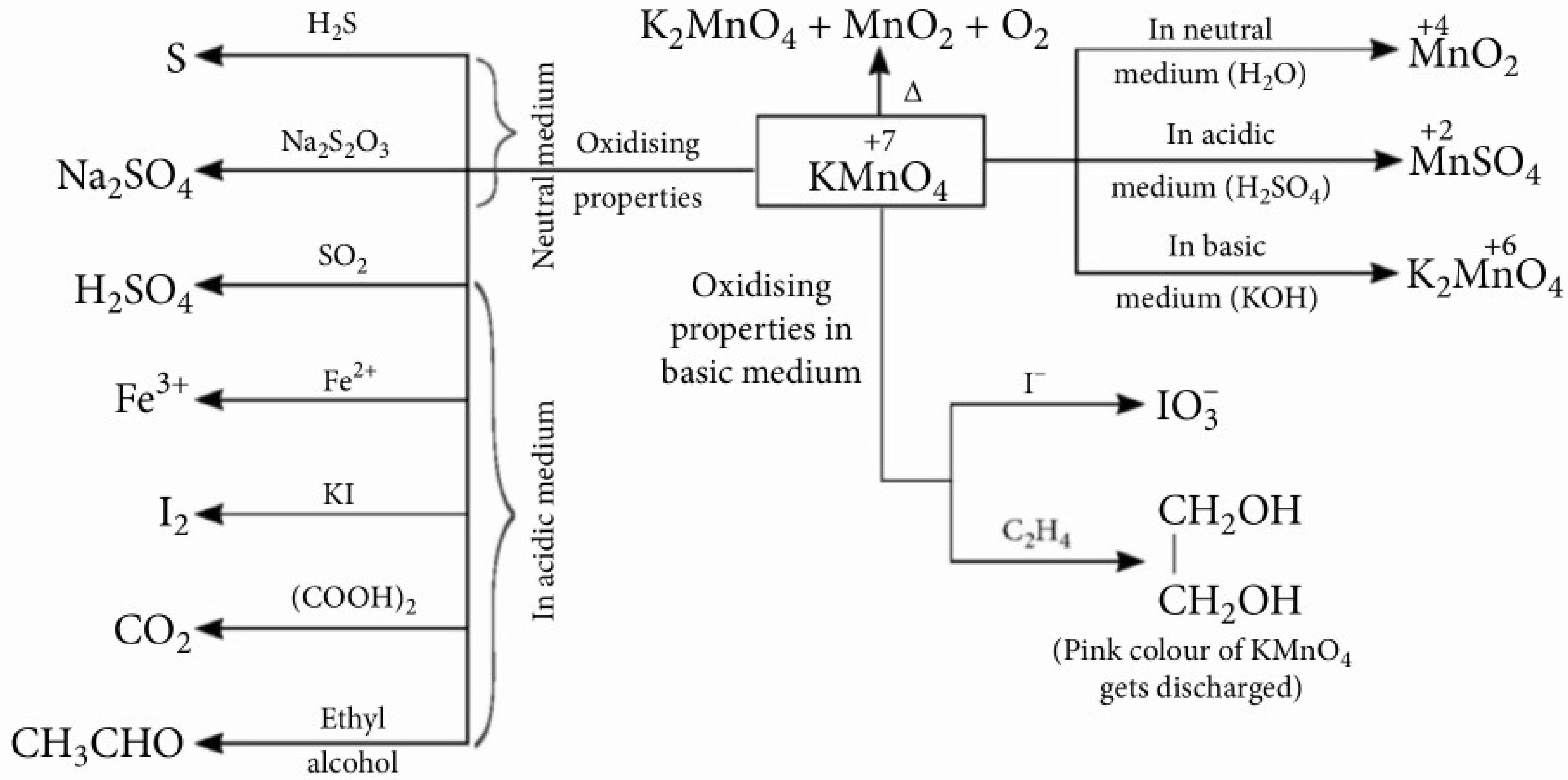
- In photography, in hardening gelating film.
- In volumetric analysis for estimation of iron and iodine in redox titrations.
- In chrome tanning in leather industry.

Potassium Permanganate ($KMnO_4$)

- **Preparation :** It is obtained from mineral pyrolusite (MnO_2).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

- **Properties :**
  - It is fairly soluble in hot water, but sparingly soluble in cold water.
  - It exists in the form of deep purple crystals which become dull in air due to superficial reduction.



Uses :

- As strong oxidising agent.
- It is used for bleaching of wool, silk and other textile fibres.
- As a disinfectant and germicide.
- Alkaline $KMnO_4$ (Baeyer's reagent) is used for detecting unsaturation in a compound.

PEEP INTO PREVIOUS YEARS

1. When neutral or faintly alkaline $KMnO_4$ is treated with potassium iodide, iodide ion is converted into '*X*'. '*X*' is
   (a) I_2 (b) IO_4^- (c) IO_3^- (d) IO^-
   (Odisha NEET 2019)

2. The correct option(s) to distinguish nitrate salts of Mn^{2+} and Cu^{2+} taken separately is (are)
   (a) Mn^{2+} shows the characteristic green colour in the flame test
   (b) only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium
   (c) only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium
   (d) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions).
   (JEE Advanced 2018)

3. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids?
(a) Mn^{2+} (b) Ti^{2+}
(c) V^{2+} (d) Cr^{2+}
(JEE Main Online 2017)

THE INNER-TRANSITION ELEMENTS (*f*-BLOCK)

- **Lanthanoids :** Last electron enters one of the 4*f*-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- **Actinoids :** Last electron enters one of the 5*f*-orbitals. Thorium (at. no. 90) to lawrencium (at. no. 103).
- **General electronic configuration :** $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

General Characteristics of Lanthanoids

Atomic and ionic radii	Decrease steadily on going from La to Lu.
Oxidation states	Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or fully-filled *f*-subshell. *e.g.*, cerium exhibits +4 oxidation state and Sm, Eu and Yb enhibit +2 oxidation state. Each lanthanoid has a tendency to acquire +3 O.S. Thus, Ce^{4+} acts as an oxidising agent and Eu^{2+}, Yb^{2+} act as strong reducing agents.
Action of air	All the lanthanoids are silvery white soft metals and tarnish readily in moist air. They burn in oxygen of air and form oxides (Ln_2O_3 type).
Coloured ions	They form coloured ions due to *f-f* transitions of unpaired electrons. La^{3+} and Lu^{3+} are colourless ions due to empty ($4f^0$) or fully-filled ($4f^{14}$) orbitals.
Magnetic properties	La^{3+}, Lu^{3+} are diamagnetic while trivalent ions of the rest of lanthanoids are paramagnetic.
Reducing agents	They readily lose electrons and are good reducing agents.
Electropositive character	Highly electropositive because of low transition energies.
Alloy formation	They form alloys easily with other metals especially iron.
Tendency to form complexes	Lanthanoids do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

- **Atomic and ionic radii (Lanthanoid contraction) :** In lanthanides there is a regular decrease in atomic radii and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.
  – **Causes :** In lanthanoids, the nuclear charge increases by one unit at each successive element and a new electron enters the 4*f*-electron by other electrons from the nuclear attraction, the size of lanthanoid atoms keep on decreasing from La to Lu. Although decrease in atomic radii is not very regular but ionic radii decreases steadily from La to Lu.
- **Consequences of lanthanoid contraction :**
  – There is decrease in basic strength of oxides and hydroxides with decrease in the size from La to Lu.
  – Similar chemical properties.
  – The electronegativity of trivalent ions increases slightly from La to Lu.
  – There is small increase in standard electrode potential values from La to Lu.

Chemical Reactivity

Ln (Lanthanoid):

$$Ln \xrightarrow{\text{Burn in } O_2} Ln_2O_3$$
$$Ln \xrightarrow{\text{Heated with S}} Ln_2S_3$$
$$Ln \xrightarrow{\text{Heated with } N_2} LnN$$
$$Ln \xrightarrow{C,\ 2500°C} LnC_2,\ Ln_3C\ \&\ Ln_2C_3$$
$$Ln \xrightarrow{H_2O} Ln(OH)_3 + H_2$$
$$Ln \xrightarrow{\text{With halogens } (X)} LnX_3$$
$$Ln \xrightarrow{\text{With dilute acid}} Ln^{3+} + H_2\uparrow$$

CONCEPT MAP

INTEGRATED RATE EQUATIONS (CHEMICAL KINETICS)

Integrated Rate Equations (For different order of reaction)

Zero Order Reaction

Features

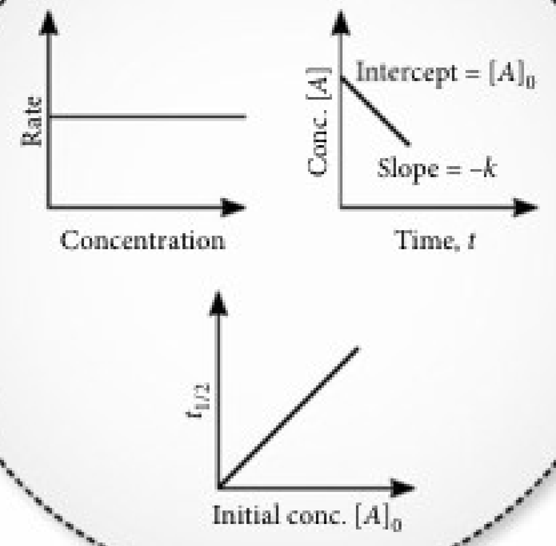
- Rate $= -\dfrac{d[A]}{dt} = k[A]^0 = k$
- $k = \dfrac{1}{t}\{[A]_0 - [A]\}$
- The concentration of the reactant decreases linearly with time, $[A]_t = [A]_0 - kt$
- Unit of k is mol L^{-1} time^{-1}.

Half Life

$$t_{1/2} = \frac{[A]_0}{2k}$$

$(t_{1/2})_{\text{zero order}} \propto [A]_0$ (initial concentration)

Graph



First Order Reaction

Features

- Rate $= -\dfrac{d[A]}{dt} = k[A]^1$
- $\ln[A]_t = -kt + \ln[A]$
- $k = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x}$
- $k = \dfrac{2.303}{t_2 - t_1}\log_{10}\dfrac{a-x_1}{a-x_2}$
- $t = \dfrac{2.303}{k}\log_{10}\dfrac{r_0 - r_\infty}{r_t - r_\infty}$
- Unit of k is time^{-1}.
- Rate of radioactive decay or disintegration, $N = N_0 e^{-kt}$

$$k = \frac{2.303}{t}\log\frac{N_0}{N}$$

Half Life

$$t_{1/2} = \frac{0.693}{k_1}$$

$\Rightarrow$ Independent of the initial concentration.

No. of half life	Conc. of reactants	Conc. of products
1	$[A_0]/2$ (50%)	$[A_0]/2$ (50%)
2	$[A_0]/4$ (25%)	$3[A_0]/4$ (75%)
3	$[A_0]/8$ (12.5%)	$7[A_0]/8$ (87.5%)
4	$[A_0]/16$ (6.25%)	$15[A_0]/16$ (93.75%)

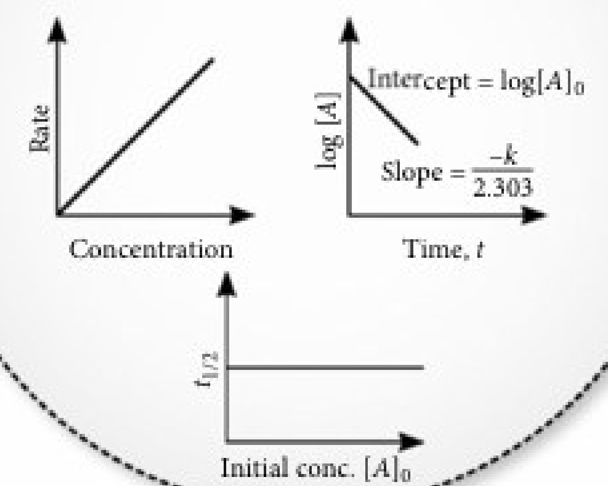
Amount left after n half lives $= \dfrac{[A]}{2^n}$

Graph

$t_{99\%} = 2 \times t_{90\%}$; $t_{99.9\%} = 3 \times t_{90\%}$

$t_{99.99\%} = 4 \times t_{90\%}$; $t_{99.9\%} = 10 \times t_{1/2}$

$t_{75\%} = 2 \times t_{50\%}$; $t_{87.5\%} = 3 \times t_{50\%}$



Second Order Reaction

Features

- Rate $= k[A]^2$ or $k[A]^1[B]^1$
- $1/[A]_t = kt + 1/[A]_0$
- When concentrations are same : $k = \dfrac{1}{t}\dfrac{x}{a(a-x)}$
- When concentrations are different : $k = \dfrac{2.303}{t(a-b)}\log_{10}\dfrac{b(a-x)}{a(b-x)}$

The change in the unit of concentration, changes the value of k here.

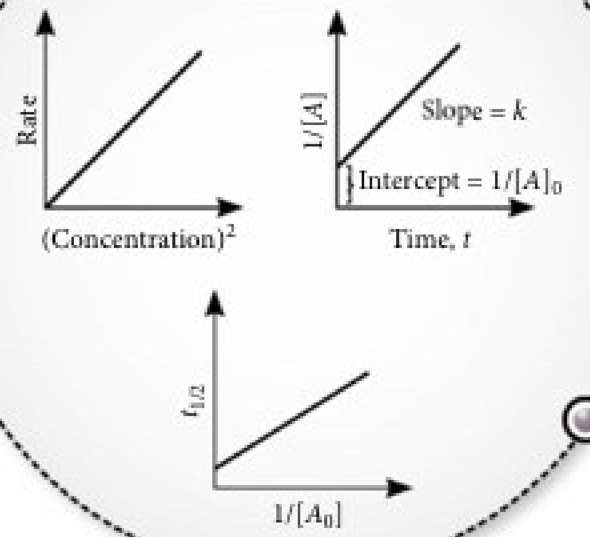
- Unit of k is L mol^{-1} time^{-1}.

Half Life

$$t_{1/2} \propto \frac{1}{[A]_0} \Rightarrow t_{1/2} = \frac{1}{k_2[A]_0}$$

No. of half life	Conc. of reactants	Conc. of products
1	$[A_0]/2$ (50%)	$[A_0]/2$ (50%)
2	$[A_0]/3$ (33.3%)	$2[A_0]/3$ (66.66%)
3	$[A_0]/4$ (25%)	$3[A_0]/4$ (75%)
4	$[A_0]/5$ (20%)	$4[A_0]/5$ (80%)

Graph



Third Order Reaction

Features

- Rate $= k[A]^3$ or $k[A]^1[B]^1[C]^1$
- $\dfrac{1}{[A]_t^2} = 2kt + \dfrac{1}{[A]_0^2}$

When concentrations are same :

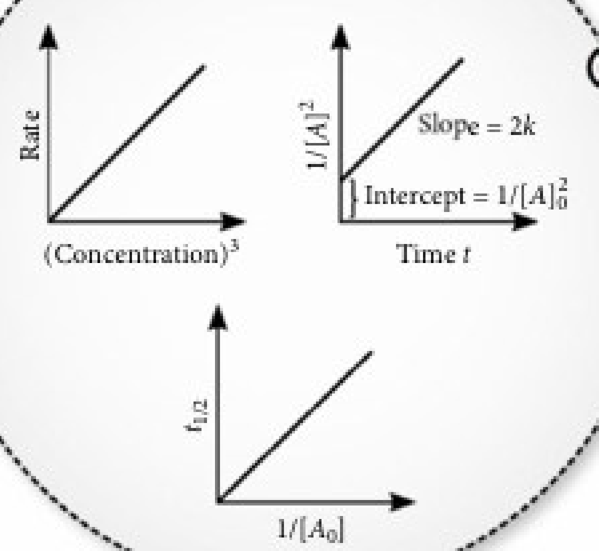
- $k = \dfrac{1}{t}\dfrac{x(2a-x)}{2a^2(a-x)^2}$
- The change in the unit of concentration changes the value of k here.
- Unit of k is L^2 mol^{-2} time^{-1}.

Half Life

$$t_{1/2} = \frac{3}{2k_3[A]_0^2}$$

$$t_{1/2} \propto \frac{1}{[A]_0}.$$

Graph



n^{th} Order Reaction

Features

- Rate $= k[A]^n$
- $k = \dfrac{1}{t(n-1)}\left[\dfrac{1}{(a-x)^{n-1}} - \dfrac{1}{a^{n-1}}\right]$

where $n \geq 2$

- Unit of k is mol^{1-n} L^{n-1} time^{-1}.

Half Life

$$t_{1/2} = \frac{2^{n-1} - 1}{k_n(n-1)[A]_0^{n-1}}$$

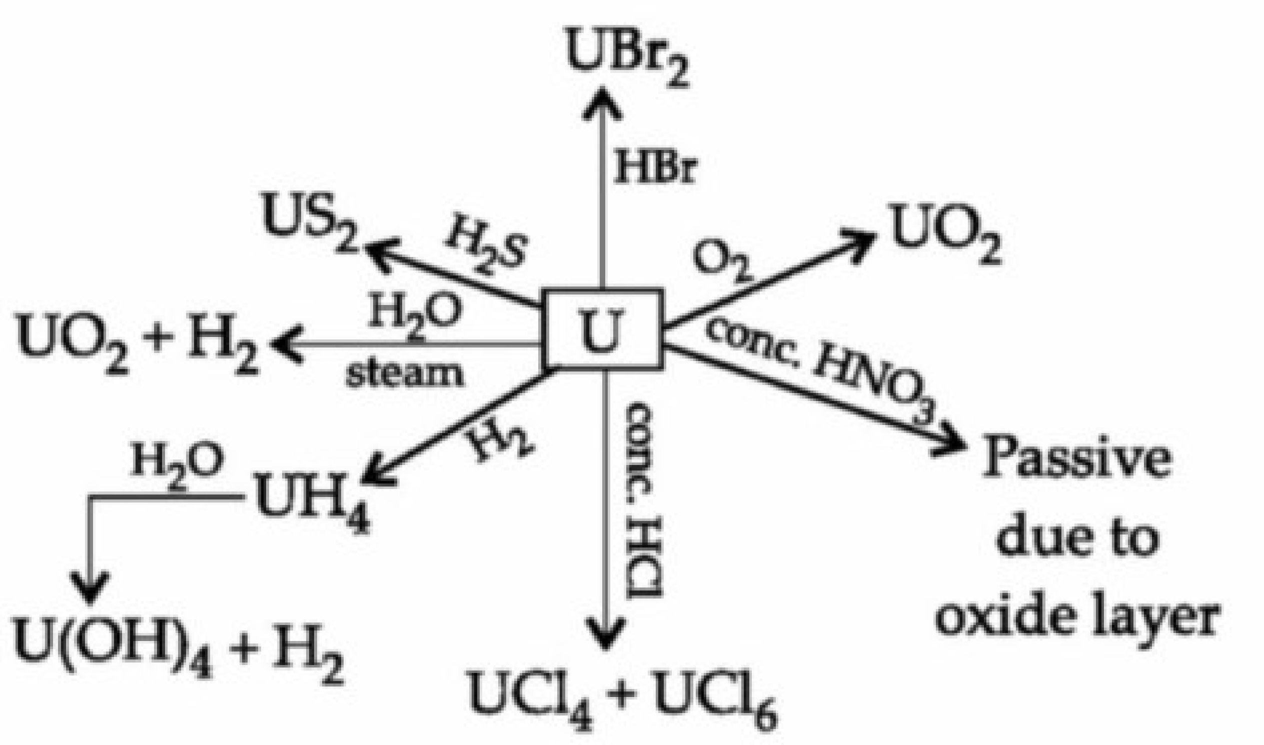
where $n \geq 2$

$$\Rightarrow t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

General Characteristics of Actinoids

Ionic radii	Like lanthanoids, ionic radii decrease regularly across the series. Actinoid contraction is greater due to poor sheilding effect of the 5*f*-electrons. Further, 5*f*-orbitals extend in space beyond 6*s* and 6*p*-orbitals whereas 4*f*-orbitals are buried deep.
Oxidation states	Like lanthanoids, most common oxidation state is +3. They also show oxidation state of +4, +5, +6 and +7, *e.g.*, in Th, Pa, U and Np respectively. They show a large number of oxidation states because of very small energy gap between 5*f*, 6*d* and 7*s* subshells.
Action of air, alkalies and acids	Like lanthanoids they are also silvery white metals, tarnish rapidly in air forming oxide coating and are not attacked by alkalies and are less reactive towards acids.
Coloured ions	Coloured due to *f-f* transition except $Ac^{3+}(5f^0)$, $Cm^{3+}(5f^7)$ and $Th^{4+}(5f^0)$ which are colourless.
Magnetic properties	They are strongly paramagnetic.
Density	All actinoids except thorium and americium have high densities.
Melting and boiling points	High melting and boiling points however there is no regular trend with rise in atomic number.
Ionisation energy	They have low ionisation energies.
Reducing agents	All actinoids are strong reducing agents.
Electropositive character	Highly electropositive metals.

Chemical Reactivity



Differences between Lanthanoids and Actinoids

	Lanthanoids	Actinoids
1.	They show +2 and +4 oxidation states in few cases besides +3.	They show higher oxidation states of +4, +5, +6 and +7 besides +3.
2.	Except promethium, they are non-radioactive.	All actinoids are radioactive.
3.	They do not form oxo-ions.	They form oxo-ions like UO_2^{2+}, PuO_2^{2+}, UO_2^{+}, etc.
4.	The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.
5.	They have less tendency of complex formation.	They have greater tendency of complex formation.

PEEP INTO PREVIOUS YEARS

4. The lanthanide ion that would show colour is
   (a) Lu^{3+} (b) Sm^{3+} (c) La^{3+} (d) Gd^{3+}
   (JEE Main 2019)

5. The reason for greater range of oxidation states in actinoids is attributed to
   (a) actinoid contraction
   (b) 5*f*, 6*d* and 7*s* levels having comparable energies
   (c) 4*f* and 5*d* levels being close in energies
   (d) the radioactive nature of actinoids.
   (NEET 2017)

6. Which one of the following statements related to lanthanons is incorrect?
   (a) Europium shows +2 oxidation state.
   (b) The basicity decreases as the ionic radius decreases from Pr to Lu.
   (c) All the lanthanons are much more reactive than aluminium.
   (d) Ce (+4) solutions are widely used as oxidizing agent in volumetric analysis.
   (NEET Phase II 2016)

Points For Extra Scoring

- Anhydrous $FeSO_4$ and $CuSO_4$ are white because of absence of ligand which causes crystal field splitting, though they have unpaired electrons.
- $Cu^{2+}(3d^9, E°_{Cu^{2+}/Cu} = 0.34V)$ is more stable than $Cu^{+}(3d^{10}, E°_{Cu^{+}/Cu} = 0.54V)$ except for the cases of large anions, *e.g.*, CuI is more stable than CuI_2, CuCN is more stable than $Cu(CN)_2$.
- $(n - 1)$ *d*-subshell is filled before *ns* subshell but when cations are formed, electrons are removed from outermost *s*-subshell instead of penultimate *d*-subshell.
- Only Os and Ru show +8 oxidation states in their compounds.
- In the oxidation reactions of $KMnO_4$ in acidic medium, only H_2SO_4 is used to produce acidic medium and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produces Cl_2 while HNO_3 itself acts as oxidising agent.
- When the trivalent ion Ln^{3+} is formed, then screening power of 4*f*- electrons is no longer equal to unity (but 0.85 since 4*f* is now penultimate shell and each time an electron is added to 4*f* orbitals), the nuclear charge increases by 0.15 and thus io nic size decreases continuously from Ce^{3+} to Lu^{3+}.
- Due to lanthanide contraction, the elements of 5*d* and 4*d*-transition series resemble each other much more closely than the elements of 4*d* and 3*d*-series.

Coordination Compounds

Addition Compounds

These are the compounds formed by combination of two or more simple compounds are called addition compounds. They are of two types :

- **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called double salt. In solution it breaks into component ions.
  e.g., $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; Potash alum
  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; Mohr's salt
  $KCl \cdot MgCl_2 \cdot 6H_2O$; Carnallite
- **Complex compound :** A compound formed by combination of two or more simple compounds which retain its identity in solid and solution states both is called complex/coordination compound.
  e.g., $K_4[Fe(CN)_6]$ Potassium ferrocyanide
  $[Cu(NH_3)_4]SO_4$ Cuprammine sulphate

Differences between double salt and coordination compound :

Double Salt	Coordination Compound
1. These exist only in solid state and dissociate into constituent species in their aqueous solution.	1. They exist in the solid state as well as in aqueous solution this is because even in the solution, the complex ion does not dissociate into ions.
2. They lose their identity in dissolved state.	2. They do not lose their identity in dissolved state.
3. In double salts' the metal atoms/ions exhibit their normal valency.	3. In coordination compounds, the metal ion satisfies its two types of valencies called primary and secondary valencies.
4. Their properties are essentially the same as those of their constituent species. For examples, potash alum shows properties of K^+, Al^{3+} etc.	4. Their properties are different from those of their constituents. For example, $K_4[Fe(CN)_6]$ does not show the test of Fe^{2+} and CN^- ions.

Werner's Theory of Coordination Compounds

- According to this theory central metal atom shows two type of linkages (valencies) in coordination compounds.
- **Primary valency :** Ionisable, corresponds to oxidation state of the central metal atom/ion, satisfied by negative ions, non-directional.
- **Secondary valency :** Non-ionisable, corresponds to coordination number of the central metal atom/ion, satisfied by neutral molecules or ligands, fixed for a metal, directional, giving definite geometry to the complex.

Terms Related to Coordination Compounds

$[Cu(NH_3)_4]SO_4$

Central metal atom
Metal atom to which ligands are attached.

Ligands
The donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond.

Counter ions
The ionizable groups written outside the brackett.

Coordination sphere
Square bracket enclosing the central atom and the ligands directly attached to it.

Coordination number
The total number of ligands attached to the central metal ion through coordinate bond.

Ligands

Chelating ligand : When a polydentate ligand coordinates to a metal ion through more than one electron pairs of donor site simultaneously, is called chelation. The resulting complex has ring like structure and such ligand is called chelating ligand.
Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.

Ambidentate Ligand : A unidentate ligand which can coordinate through two different atoms. *e.g.*, NO_2^-, SCN^-, etc.

Mono or unidentate ligands : Ligands with one donor site. *e.g.*, F^-, Cl^-, Br^-, H_2O, CN^-, NO_2^-, OH^-, CO, etc.

Bidentate ligands : Ligands which have two donor atoms at two positions.
e.g., Ethylenediammine $(NH_2CH_2CH_2NH_2)$, oxalate $(C_2O_4^{2-})$, glycinate $CH_3\langle^{NH_2}_{COO^-}$, etc.

Polydentate ligands : The ligands having several donor atoms are called polydentate ligands. *e.g.*, Diethylenetriammine having 3 donor atoms is tridentate, EDTA with 6 donor atoms is hexadentate.

IUPAC Nomenclature

Rules for Naming Coordination Compounds

- The cation is named first then the anion.
- In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
- Name of anionic ligands end in –*o*. *e.g*, Cl^- : Chlorido, $C_2O_4^{2-}$: Oxalato etc.
- Neutral ligands (with a few exceptions *e.g.*, H_2O : aqua) retain their names *e.g.*, NH_3 : Ammine etc.
- Name of cationic ligands end in – *ium*. *e.g.*, NO_2^+ : Nitronium etc.
- Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. *e.g.*, ethylenediamine (*en*).
- Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
  e.g., —SCN (Thiocyanato-S or Thiocyanato), —NCS (Thiocyanato-N or Isothiocyanato), —ONO (Nitrito-O or Nitrito), —NO_2 (Nitrito-N or Nitro)

Isomerism in Coordination Compounds

- Two or more substances having the same molecular formula but different structural or spatial arrangement are called isomers and phenomenon is called isomerism.

Isomerism

- **Structural Isomerism**
- **Stereoisomerism**

Structural Isomerism

Ionisation isomerism

Compounds, which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called ionisation isomers. *e.g.*, $[CoBr(NH_3)_5]SO_4$ and $[Co(NH_3)_5SO_4]Br$

Hydrate isomerism

Isomers, which differ in the number of water molecules attached to the metal atom or ion as ligands.
e.g., $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$

Linkage isomerism

When an ambidentate ligand attached to metal through different atoms than the compounds are said to be linkage isomers.
e.g., $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$

Coordination isomerism

When both positive and negative ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions.
e.g., $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(CN)_6][Cr(NH_3)_6]$

Stereoisomerism

*** Geometrical or *cis-trans* isomerism**

If two identical ligands occupy adjacent positions ⇒ *cis*
If occupy opposite positions ⇒ *trans*

- **In Square Planar C.N. : 4**
  Shown by
  MA_2X_2
  $M(AB)X_2$
  MA_2XY
  $MABXY$
- **In Octahedral C.N. : 6**
  Shown by
  - $M(AA)_2X_2$ and MA_4X_2
    - *cis*
    - *trans*
  - MA_3X_3
    - If all three similar groups occupy adjacent position at the corners of octahedral face then *fac*-isomer
    - If three similar groups present around meridian of octahedron then *mer*-isomer

Optical isomerism

This isomerism arises due to non-superimposable mirror images.

Common in octahedral complexes with 2 or 3 bidentate ligands.

- *cis*-optically active
  - *d*-form
  - *l*-form
- *trans*-optically inactive

* Geometrical isomerism is not shown by tetrahedral complexes.

Peep Into Previous Years

7. The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is
(a) geometrical isomerism
(b) coordination isomerism
(c) ionization isomerism
(d) linkage isomerism.
(NEET 2018)

8. As per IUPAC norms, the name of the complex $[Co(en)_2(ONO)Cl]Cl$ is
(a) Chlorido*bis*(ethane-1,2-diamine)nitro-O-cobalt (III) chloride
(b) Chloro*bis*(ethylenediamine)nitro-O-cobalt(III) chloride
(c) Chloridodi(ethylenediamine)nitrocobalt(III) chloride
(d) Chloroethylenediaminenitro-O-cobalt (III) chloride.
(Karnataka CET 2016)

9. The correct statement on the isomerism associated with the following complex ions,
(1) $[Ni(H_2O)_5(NH_3)]^{2+}$ (2) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and (3) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is
(a) (1) and (2) show only geometrical isomerism
(b) (1) and (2) show geometrical and optical isomerism
(c) (2) and (3) show geometrical and optical isomerism
(d) (2) and (3) show only geometrical isomerism.
(JEE Main Online 2015)

Bonding in Coordination Compounds

Valence Bond Theory (VBT)

- It was developed by Pauling.
  - A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
  - Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon the total number of ligands.
  - The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.
  - Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
  - Paramagnetism $\propto$ No. of unpaired electrons.
  - Magnetic moment $=\sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

Coordination Number	Type of Hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where $X = Cl^-$, Br^-, I^-
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

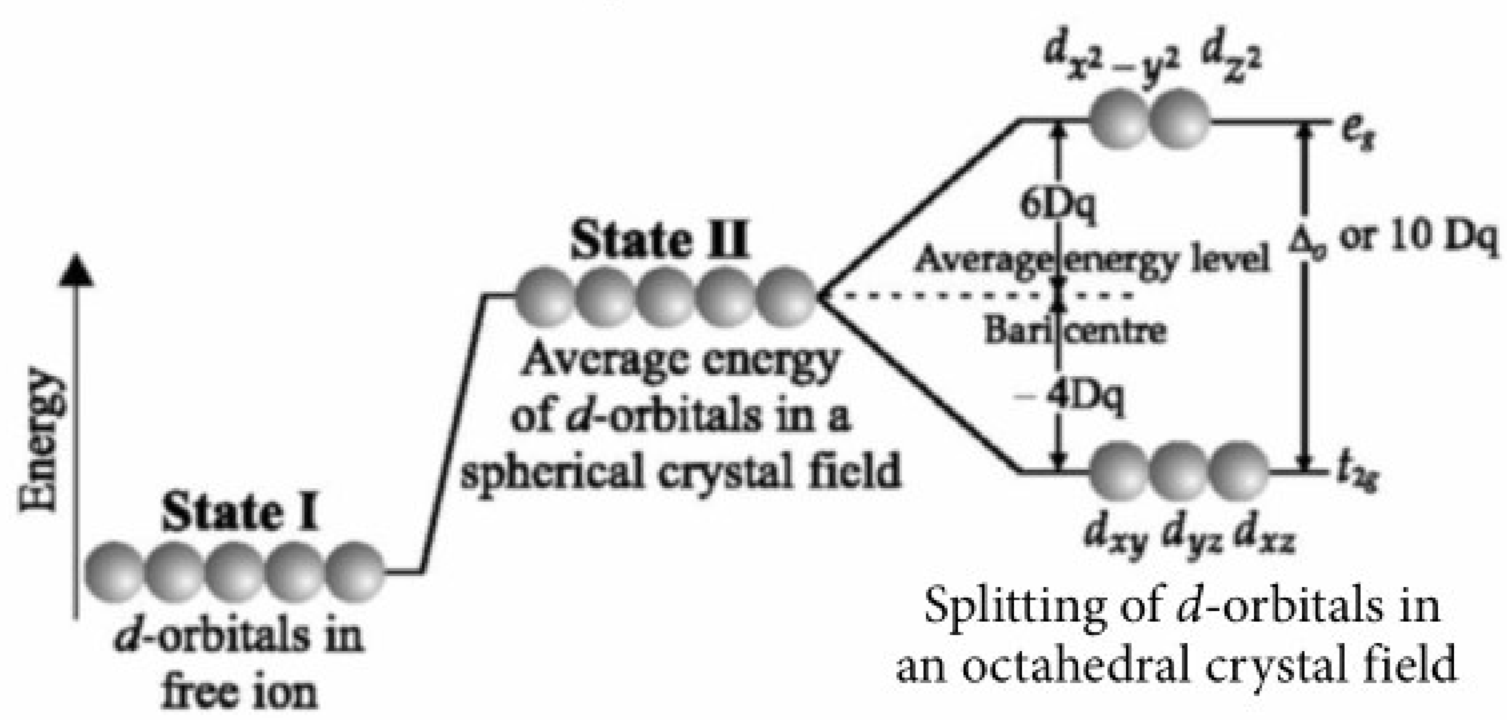
Differences between Inner Orbital Complexes and Outer Orbital Complexes

Inner Orbital Complexes	Outer Orbital Complexes
Involves inner *d*-orbitals *i.e.*, $(n-1)d$-orbitals.	Involves outer *d*-orbitals *i.e.*, *nd*-orbitals
Low spin complexes	High spin complexes
Have less or no unpaired electrons, *e.g.*, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. *e.g.*, $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

Crystal Field Theory (CFT)

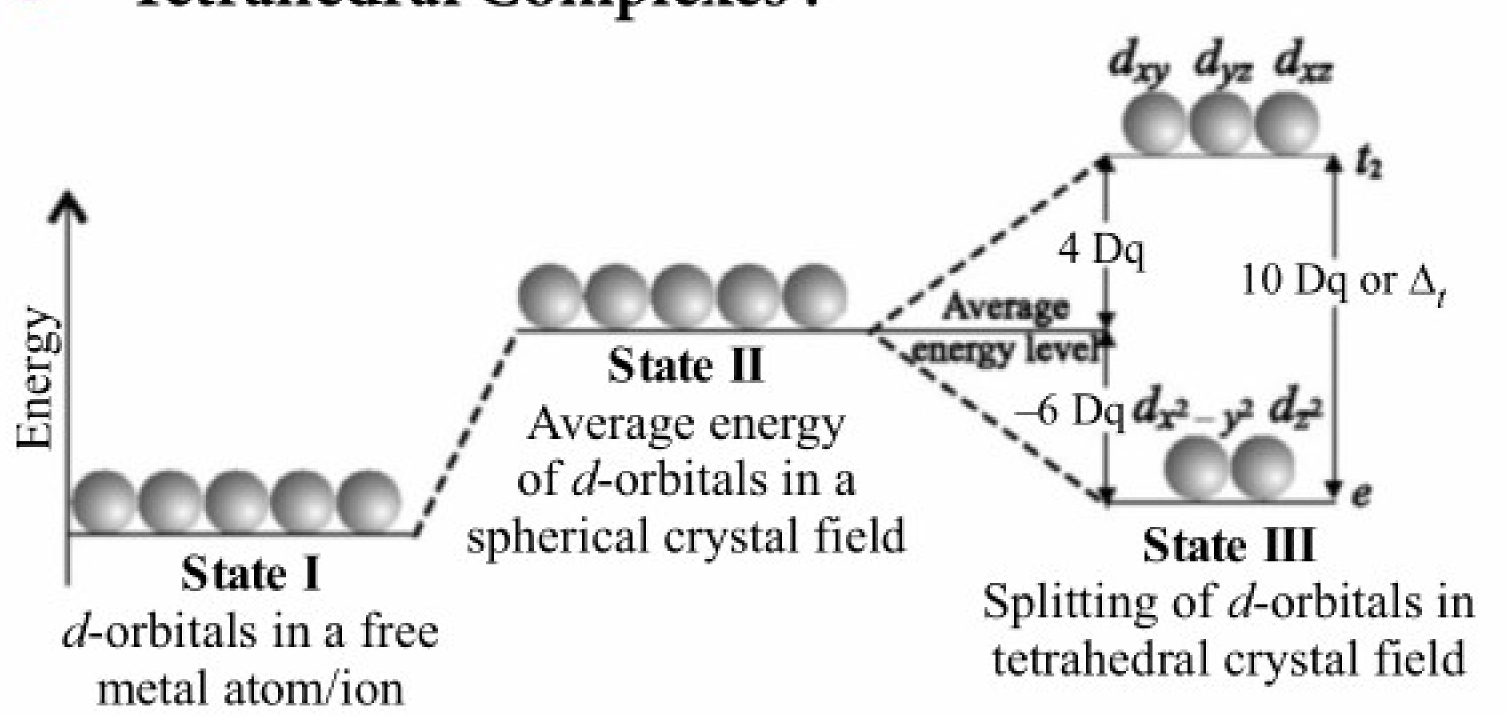
It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength. Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.

- **Octahedral Complexes :**



Splitting of *d*-orbitals in an octahedral crystal field

- **Tetrahedral Complexes :**



Splitting of *d*-orbitals in tetrahedral crystal field

  - If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.

– If $\Delta_o > P$, then pairing of electrons takes place and a low spin complex is formed.
– Difference in energy between e and t_2 level is less in tetrahedral complexes, $\Delta_t = \frac{4}{9}\Delta_o$

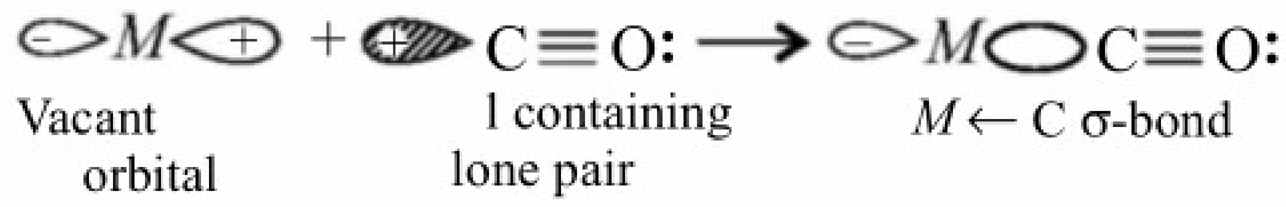
Spectrochemical Series

- Ligands are arranged in the order of increasing field strength called spectrochemical series.
- $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

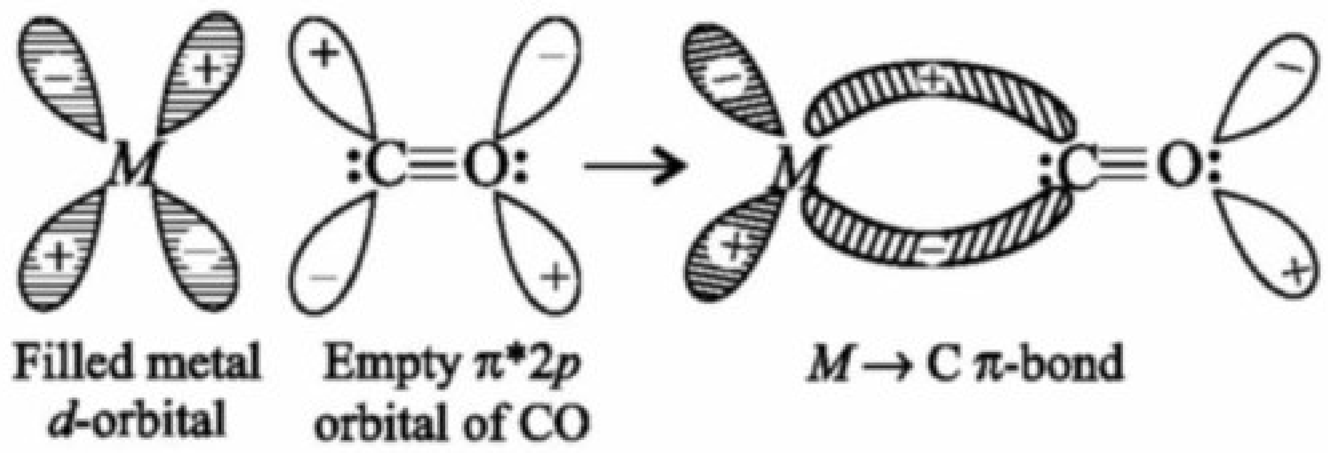
Weak field ligand → Increasing order of CFSE → Strong field ligand

Bonding in Metal Carbonyls

- Metal–carbon bond in metal carbonyls possesses both σ- and π-character. Its formation involves following steps :
- There is an overlap of filled π_{2p} orbital of CO with suitable empty metal orbital resulting in the formation of σ- bond.



- π-overlap involving filled metal d-orbital and empty antibonding π^*2p orbital of same CO. This results in formation of $M \rightarrow C$ π-bond. This is also called back bonding.



Stability of Coordination Compounds

Stability depends on

- **Charge on the central metal ion (oxidation state) :** Greater the charge on central metal ion, more is the stability.
- **Basic nature of ligand :** More the basic strength of ligand, more is the stability of complex.
- **Presence of chelate rings :** Formation of chelate ring increases the stability of complex.
- **Size of the metal ion :** Smaller the size of metal ion, more is the stability.
- **Electronegativity and polarising power of the central metal ion :** More is the electronegativity and polarising power of the metal ion, more stable is the complex.

Applications of Coordination Compounds

- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordinate compounds of Mg, Fe and Co respectively.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.
- *cis*-Platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalyst.

Peep Into Previous Years

10. What is the correct electronic configuration of the central atom in $K_4[Fe(CN)_6]$ based on crystal field theory?

(a) $e^4t_2^2$ (b) $t_{2g}^4e_g^2$ (c) $t_{2g}^6e_g^0$ (d) $e^3t_2^3$

(NEET 2019)

11. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)
(Atomic numbers: Fe = 26, Ni = 28)

(a) total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16
(b) these are predominantly low spin in nature
(c) metal–carbon bond strengthens when the oxidation state of the metal is lowered
(d) the carbonyl C — O bond weakens when the oxidation state of the metal is increased.

(JEE Advanced 2018)

12. The correct order of spin-only magnetic moments among the following is
(Atomic number : Mn = 25, Co = 27, Ni = 28, Zn = 30)

(a) $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$
(b) $[CoCl_4]^{2-} > [MnCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$
(c) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$
(d) $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

(JEE Main Online 2018)

POINTS FOR EXTRA SCORING

- Different complexes exhibit different colours when either the metal ion is different or the metal ion is same but the ligands attached to it are different.
- **Effective Atomic Number Rule (EAN Rule) :** EAN = Atomic No. of metal – No. of electrons lost in ion formation + No. of electrons gained from ligands
- **Irving–Williams order :** Irrespective of the nature of the ligand, the stability of the divalent metal ions of the first transition series is in the following order : Mn (II) < Fe (II) < Co (II) < Ni (II) < Cu (II) < Zn (II)
- **Calculation of CFSE :** CFSE = $(-0.4x + 0.6y)\,\Delta_o$
  where, x = No. of electrons in t_{2g}
  y = No. of electrons in e_g
- **In octahedral complexes**
  Strong field ligand $\longrightarrow$ High Δ_o value $\longrightarrow$ Low spin complexes
  Weak field ligand $\longrightarrow$ Low Δ_o value $\longrightarrow$ High spin complexes
- Colour of the coordination compound is due to $d-d$ transition.
- Large Δ_o = higher energy light absorbed (shorter wavelengths)
  Smaller Δ_o = lower energy light absorbed (longer wavelengths)
- Chelating ligands give much larger values of stability constant.
- The numerical value of stability constant is a measure of stability of the complex in solution, greater the magnitude of the stability constant more stable is the complex.

Answer Key For Peep Into Previous Years

1.	(c)	2.	(b,d)	3.	(a)	4.	(b)	5.	(b)	6.	(c)
7.	(a)	8.	(a)	9.	(a)	10.	(c)	11.	(b,c)	12.	(c)

WRAP it up!

1. Anhydrous ferric chloride is prepared by
   (a) heating hydrated ferric chloride at a high temperature in a stream of air
   (b) heating metallic iron in a stream of dry chlorine gas
   (c) reaction of ferric oxide with hydrochloric acid
   (d) reaction of metallic iron with dilute hydrochloric acid.

2. If the lanthanoid ion (M^{3+}) with $x\,f$-electrons has a pink colour, then the lanthanoid ion with $(14-x)f$-electrons will have the colour as
   (a) blue (b) red (c) green (d) pink.

3. Mixture X containing 0.02 mol of $[Co(NH_3)_5SO_4]Br$ and 0.02 mol of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 litre of solution.
   1 litre of mixture X + excess $AgNO_3 \longrightarrow Y$
   1 litre of mixture X + excess $BaCl_2 \longrightarrow Z$
   Number of moles of Y and Z are respectively
   (a) 0.01, 0.01 (b) 0.02, 0.01
   (c) 0.01, 0.02 (d) 0.02, 0.02

4. Which of the following complexes exists as pair of enantiomers?
   (a) *trans*-$[Co(en)_2Cl_2]^+$
   (b) $[Co(NH_3)_4Cl_2]^+$
   (c) $[Co\{P(C_2H_5)_3\}_2ClBr]$
   (d) $[Cr(en)_3]^{3+}$

5. CrO_3 dissolves in aqueous NaOH to give
   (a) CrO_4^{2-} (b) $Cr(OH)_3$
   (c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

6. When copper sulphate solution is added to potassium ferrocyanide, the formula of product obtained is
   (a) $Cu_2[Fe(CN)_6]$ (b) $Cu(CN)_3$
   (c) $CuFe(CN)_6$ (d) $Cu(CN)_2$

7. The coordination number of a central metal atom/ion in a complex is determined by
(a) the number of ligands around a metal atom/ion bonded by sigma bonds
(b) the number of only anionic ligands bonded to the metal atom/ion
(c) the number of ligands around a metal atom/ion bonded by both sigma and pi-bonds
(d) the number of ligands around a metal atom/ion bonded by pi-bonds.

8. Which of the following pair contains metals in their highest oxidation states?
(a) MnO_2, TiO_3
(b) $[MnO_4]^-$, CrO_2Cl_2
(c) $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$
(d) $[NiCl_4]^{2-}$, $[CoCl_4]^-$

9. Which one of the following cyano complex would exhibit the lowest value of paramagnetic behaviour?
(a) $[Cr(CN)_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Mn(CN)_6]^{3-}$

10. Low spin complex of d^6-cation in an octahedral field will have the following energy
(Δ_o = crystal field splitting energy in an octahedral field, P = electron pairing energy)
(a) $\frac{-12}{5}\Delta_o + P$ (b) $\frac{-12}{5}\Delta_o + 3P$
(c) $\frac{-2}{5}\Delta_o + 2P$ (d) $\frac{-2}{5}\Delta_o + P$

11. **Assertion :** F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

12. The colourless species is
(a) VCl_3 (b) $VOSO_4$
(c) Na_3VO_4 (d) $[V(H_2O)_6SO_4]H_2O$

13. Copper sulphate is dissolved in water containing _________ for making Bordeaux mixture.
(a) NaOH (b) KCN
(c) $Ca(OH)_2$ (d) all of these

14. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is
(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight.

15. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solution but not in acidic solution. What is the reason for it?
(a) In acidic solutions hydration protects copper ions.
(b) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available.
(c) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali.
(d) Copper hydroxide is an amphoteric substance.

16. Which of the following does not have a metal-carbon bond?
(a) $K[Pt(C_2H_4)Cl_3]$ (b) $Ni(CO)_4$
(c) $Al(OC_2H_5)_3$ (d) C_2H_5MgBr

17. The EAN of metal atoms in $K_3[Cr(C_2O_4)_3]$ and $Co_2(CO)_8$ respectively are
(a) 34, 35 (b) 34, 36 (c) 33, 36 (d) 36, 35

18. A white crystalline salt *A* reacts with dilute HCl to liberate a suffocating gas *B* and also forms a yellow precipitate. The gas *B* turns potassium dichromate acidified with dilute H_2SO_4 to a green coloured solution *C*. *A*, *B* and *C* are respectively
(a) Na_2SO_3, SO_2, $Cr_2(SO_4)_3$
(b) $Na_2S_2O_3$, SO_2, $Cr_2(SO_4)_3$
(c) Na_2S, SO_2, $Cr_2(SO_4)_3$
(d) Na_2SO_4, SO_2, $Cr_2(SO_4)_3$

19. The correct IUPAC name of the compound $[Cr(NH_3)_5(NCS)]\,[ZnCl_4]$, is
(a) pentaammineisothiocyanatochromium(III) tetrachloridozincate(II)
(b) pentaammineisothiocyanatozinc(II) chloridochromate(III)

Monthly Test Drive CLASS XI ANSWER KEY

1. (c)	2. (c)	3. (b)	4. (a)	5. (a)
6. (d)	7. (c)	8. (d)	9. (a)	10. (b)
11. (d)	12. (c)	13. (a)	14. (c)	15. (a)
16. (b)	17. (a)	18. (d)	19. (a)	20. (b,c,d)
21. (a,b)	22. (b,d)	23. (a,b,c)	24. (4)	25. (2)
26. (5)	27. (a)	28. (d)	29. (d)	30. (a)

(c) pentaammineisothiocyanatochromate(II) tetrachloridozincate(II)

(d) isothiocyanatopentaamminechromium(II) chloridozinc(IV).

20. When AgCl is treated with KCN

(a) Ag is precipitated

(b) a complex ion is formed

(c) double decomposition takes place

(d) no reaction takes place.

SOLUTIONS

1. (b): Anhydrons $FeCl_3$ cannot be prepared by heating hydrated salt, because it decomposes to Fe_2O_3 on heating.

Reaction of ferric oxide with hydrochloric acid gives hydrated $FeCl_3$.

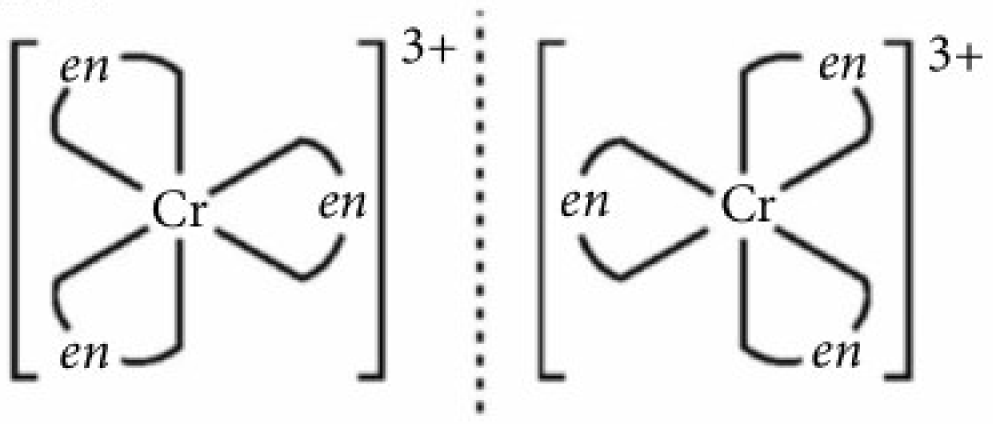
Reaction of metallic iron with dilute HCl produces $FeCl_2$ and H_2.

2. (d): In case of lanthanoids M^{3+} ion, the element with xf electrons has a similar colour to that of $(14 - x)f$ electrons.

3. (a) : $\underset{0.01\ \text{mol/L}}{[Co(SO_4)(NH_3)_5]Br} + \underset{\text{from } AgNO_3}{Ag^+(\text{excess})} \rightarrow [Co(SO_4)(NH_3)_5]^+ + \underset{0.01\ \text{mol}}{AgBr_{(s)}}$

$\underset{0.01\ \text{mol/L}}{[CoBr(NH_3)_5]SO_4} + \underset{\text{from } BaCl_2}{Ba^{2+}_{(aq)}} \rightarrow [CoBr(NH_3)_5]^{2+} + \underset{0.01\ \text{mol}}{BaSO_{4(s)}}$

4. (d): Optical isomers rarely occur in square planar complexes on account of presence of axis of symmetry. Optical isomerism is very common in octahedral complexes of the formula, $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef\,]^{n\pm}$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$ and $[M(AB)_3]^{n\pm}$. Thus, among the given compounds, only $[Cr(en)_3]^{3+}$ exhibits optical isomerism and exists as a pair of enantiomers.



5. (a) : $CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$

6. (a) : $2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Reddish brown ppt.}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$

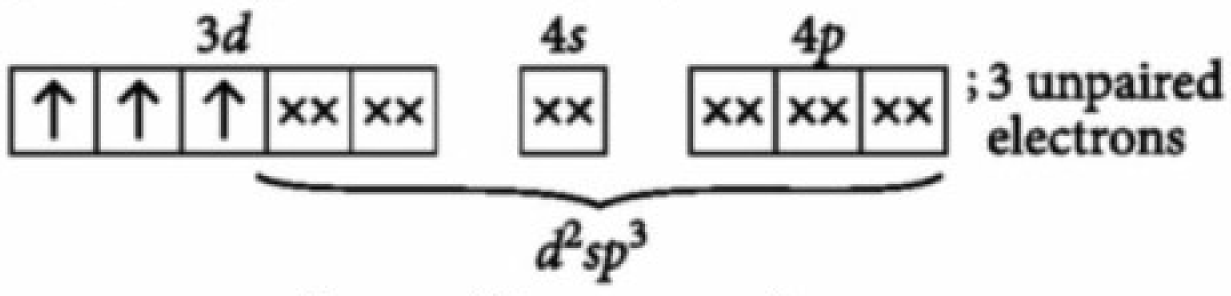
7. (a) : The coordination number of the central atom or ion is determined by the number of sigma bonds between the ligands and the central atom/ion.

8. (b): The oxidation states of Mn in MnO_4^- is +7 and Cr in CrO_2Cl_2 is +6.

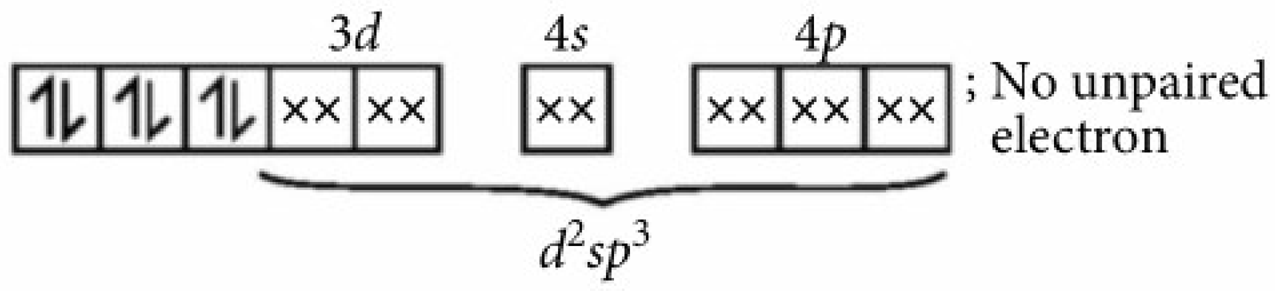
So, the pair $[MnO_4]^-$, CrO_2Cl_2 has the metals in their highest oxidation states.

9. (b): CN^- is a strong field ligand, thus, causes pairing of electrons in $3d$-orbitals.

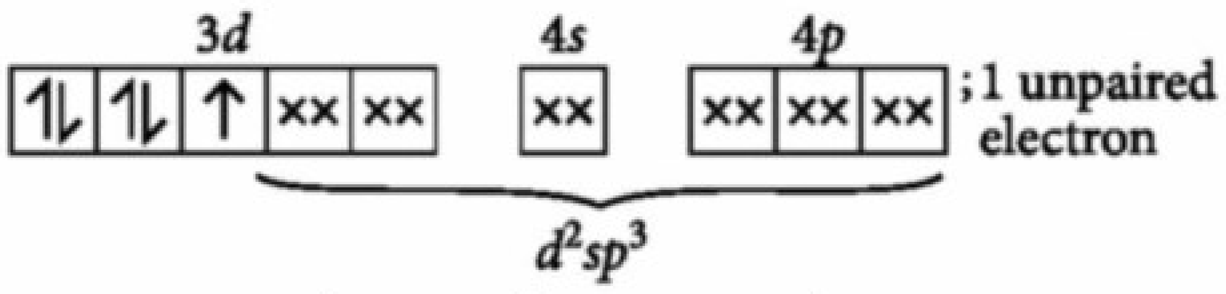
$[Cr(CN)_6]^{3-}$: Cr^{3+} : $[Ar]3d^3$



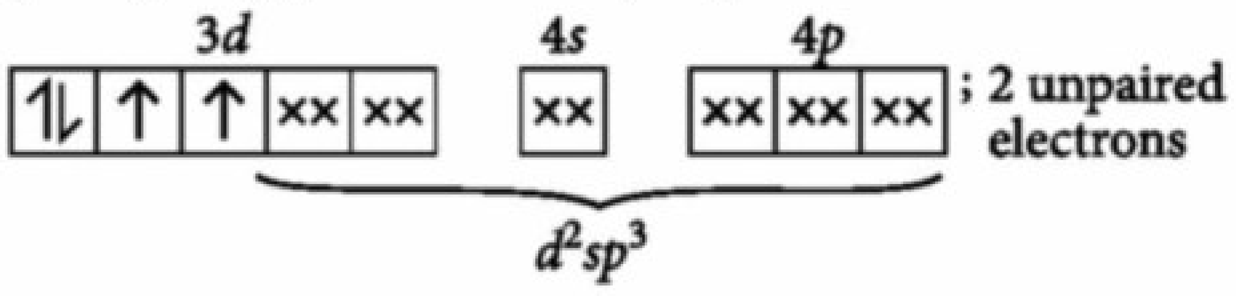
$[Co(CN)_6]^{3-}$: Co^{3+} : $[Ar]3d^6$



$[Fe(CN)_6]^{3-}$: Fe^{3+} : $[Ar]3d^5$



$[Mn(CN)_6]^{3-}$: Mn^{3+} : $[Ar]3d^4$



Greater the number of unpaired electrons, higher is the paramagnetism.

10. (b): C.F.S.E. $= (-0.4x + 0.6y)\Delta_o + zP$

where x = number of electrons occupying t_{2g} orbital

y = number of electrons occupying e_g orbital

z = number of pairs of electrons

For low spin d^6 complex electronic configuration

$= t_{2g}^6\, e_g^0$ or $t_{2g}^{2,2,2}\, e_g^0$

$\therefore\ x = 6, y = 0, z = 3$

C.F.S.E. $= (-0.4 \times 6 + 0 \times 0.6)\Delta_o + 3P = \frac{-12}{5}\Delta_o + 3P$

11. (a)

12. (c) : Na_3VO_4 contains vanadium in +5 oxidation state which has empty d-orbitals and is thus colourless.

13. (c) : Bordeaux mixture consists of copper sulphate ($CuSO_4$) and slaked lime $[Ca(OH)_2]$.

14. (b): Potassium dichromate is used to standardise sodium thisulphate solution. In acidic solution, $K_2Cr_2O_7$

Quotable Quote

I don't care that they stole my idea ...
I care that they don't have any of their own.

NIKOLA TESLA

oxidises KI to iodine, the iodine thus generated can then be titrated with thiosulphate solution using starch indicator.

$$\overset{+6}{Cr_2}O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$\therefore$ Equivalent weight of $K_2Cr_2O_7 = \dfrac{\text{Molecular weight}}{6}$

15. (b): : NH_3 molecule acts as a base due to the presence of a lone pair of electrons on it. In acidic medium, it accepts a proton to form NH_4^+ ion, hence it does not have a lone pair of electrons on N-atom. Therefore, it cannot act as a ligand.

$$:NH_3 + H^+ \longrightarrow NH_4^+$$

16. (c) : In $Al(OC_2H_5)_3$, aluminium atom is bonded to C_2H_5 group through oxygen.

17. (c) : $K_3[Cr(C_2O_4)_3]$; EAN = (24 – 3) + 6 × 2 = 33

$Co_2(CO)_8$; EAN = 27 + 1 (1 electron shared from another Co atom) + 8 (8 electrons from 4 CO molecules) = 36

18. (b): Dilute HCl decomposes $Na_2S_2O_3(A)$ with evolution of a gas which possesses a suffocating smell of burning sulphur *i.e.*, $SO_2(B)$ and yellow ppt. of sulphur is obtained.

$$\underset{(A)}{Na_2S_2O_3} + 2HCl \longrightarrow 2NaCl + \underset{(B)}{SO_2\uparrow} + \underset{\text{(Yellow ppt.)}}{S\downarrow} + H_2O$$

When acidified potassium dichromate paper is exposed to the gas, it attains a green colour due to the formation of chromium sulphate.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\substack{(C)\\ \text{Green}}}{Cr_2(SO_4)_3} + H_2O$$

19. (a)

20. (b): $AgCl + 2KCN \longrightarrow KAg[(CN)_2] + KCl$

Science Behind Indian Customs

Do not take bath immediately after eating

If a person is immediately taking bath after a meal, the digestion process gets slowed down as cold water activates certain chemicals in the body that rushes the blood to the skin to keep it warm and the digestion process takes a backseat. Bath will increase blood flow to the hands, feet and body because of which the amount of blood around the stomach will continue to decrease. This will weaken the digestive system in our stomach. So, it was always advised by our ancestors to take food after having a bath.

The act of putting water around the plate

We know water acts as a repellent to many tiny creatures that roam on the floor seen and unseen, hence the circle of water stops them to approach the plate when kept on the floor. Also they are attracted towards the part of food kept outside the plate for birds as per the Indian customs, thus making it safe to consume our food. This practice is redundant while eating on dining table which is presumable cleaner than the floor. Those who still practice it on table are just following tradition without knowing the meaning behind it.

Why do elders rotate crystal salt, lemon around head to prevent from an evil eye?

An evil eye (negative energy) creates unwanted magnetic field around us which affect our health. Salt can be considered as the first antibiotic. Not only that, the salty and acidic substances have the properties to keep away from these unwanted magnetic field. When the sat and lemon revolved around a person,it forms an aura layer of antibiotics and would kill all the bacteria. Not only has this, revolving around the person balance the magnetic field too. This would make the person feel better.

Scientific reason behind hanging leaves on doors

It is common practice in india to decorate the main door of the house, temples with a garland of leaves. It may just be a ritual but there is a more scientific meaning behind the hanging of these leaves. The garland is made preferably of fresh and green mango leaves for their aesthetically pleasing appearance but neem leaves are also included most of the time. As we know, green leaves absorb carbon dioxide and release oxygen. This helps in keeping the surrounding atmosphere clean and hygienic. The green colour is also soothing and refreshing to the mind. Having a garland of leaves at the doorstep can be a small way of relaxing and unwinding from stress.

CBSE warm-up!

CLASS-XII

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 5

Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Section A : Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
(iii) Section B : Q. no. 21 to 27 are short answer questions and carry 2 marks each.
(iv) Section C : Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
(v) Section D : Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
(vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
(vii) Use log tables if necessary, use of calculator is not allowed.

SECTION - A

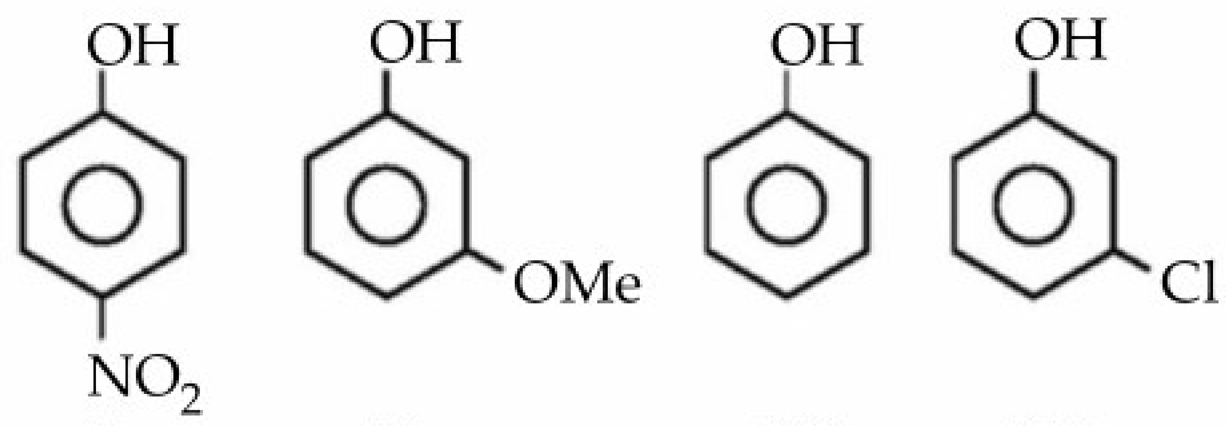
1. In S_N2 substitution reaction of the type,
$R - Br + Cl^- \xrightarrow{DMF} R - Cl + Br^-$
which one of the following has the highest relative rate?

(a) $\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_2Br \\ | \\ CH_3 \end{array}$ (b) CH_3CH_2Br

(c) $CH_3CH_2CH_2Br$ (d) $\begin{array}{c} CH_3 - CH - CH_2Br \\ | \\ CH_3 \end{array}$

2. Conversion of chlorobenzene to phenol involves
(a) electrophilic substitution
(b) nucleophilic substitution
(c) free radical substitution
(d) electrophilic addition.

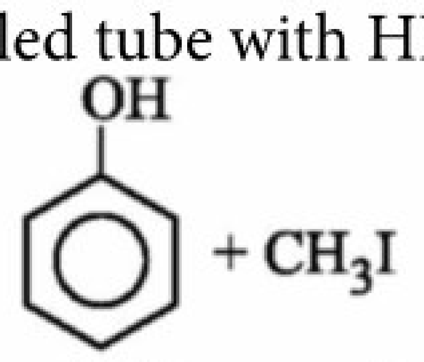
3. The correct increasing order of reactivity for the given molecules towards electrophilic aromatic substitution is

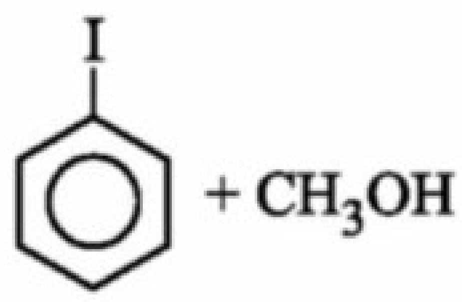


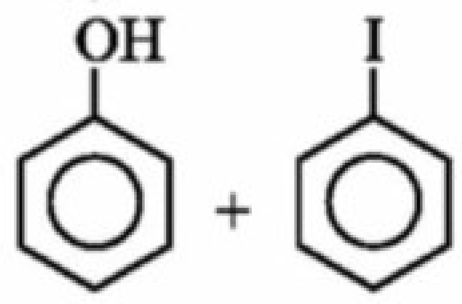
(I) (II) (III) (IV)

(a) I < IV < II < III (b) I < IV < III < II
(c) I < III < II < IV (d) I < III < IV < II

4. The products obtained when anisole is heated in a sealed tube with HI are

(a) 

(b) 

(c) 

(d) $CH_3OH + CH_3I$

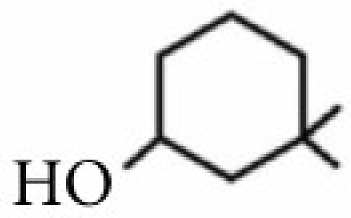
5. Which of the following compounds on oxidation gives ethyl methyl ketone?
(a) 2-propanol (b) 1-butanol
(c) 2-butanol (d) t-butyl alcohol

6. An ether is more volatile than an alcohol having the same molecular formula. This is due to
(a) dipolar character of ethers
(b) alcohols having resonance structures
(c) intermolecular hydrogen bonding in ethers
(d) intermolecular hydrogen bonding in alcohols.

7. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is
(a) 2 (b) 3 (c) 4 (d) 1

8. Chloroform on reaction with conc. HNO_3 gives
(a) chloropicrin (b) nitromethane
(c) picric acid (d) acetylene.

9. $R-CH_2-Br + AgCN \xrightarrow{\text{alcohol}} Z$ (Major product)
The product Z may be
(a) $R-CH_2-CN$ (b) $R-CH_2-NC$
(c) $R-CH_2-CH_2-CN$ (d) $R-CH_2-CH_2-NC$

10. The IUPAC name of the compound,  is
(a) 3,3-dimethyl-1-hydroxy cyclohexane
(b) 1,1-dimethyl-3-hydroxy cyclohexane
(c) 3,3-dimethyl-1-cyclohexanol
(d) 1,1-dimethyl-3-cyclohexanol.

11. Arrange the following halides in order of increasing S_N2 reactivity.
CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

12. Identify the major product of the following reaction
Me —  — I + Cu $\xrightarrow{\Delta}$

13. Explain the following :
Alkyl halides, though polar, are immiscible with water. *(AI 2017C, Foreign 2015, Delhi 2013C, AI 2013C, 2012C, 2010C)*

14. Suggest the most probable product of the following reaction :
$$CH_3-CH=CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH]{\text{(i) } B_2H_6}$$

15. What happens when benzenesulphonic acid is fused with NaOH followed by hydrolysis?

16. Write the IUPAC name of the given compound.
$$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-OH$$
(AI 2015)

17. Predict the product.
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + CH_3ONa \longrightarrow$$

18. What is the order of dehydration of 1°, 2° and 3° alcohols?

19. Why CHF_3 is less acidic than $CHCl_3$ though fluorine is more electronegative than chlorine?

20. What will be the order of boiling points of different alkyl halides containing same alkyl group?

SECTION - B

21. Haloarenes are less reactive than haloalkanes. Explain.

22. How do you convert :
(i) Chlorobenzene to biphenyl
(ii) 2-Bromobutane to but-2-ene?

23. How are the following conversions carried out :
(i) Benzyl chloride to benzyl alcohol
(ii) Propene to 1-iodopropane ?

24. How is methanol manufactured? Give one use of methanol.

25. Give reasons :
(i) Racemic mixture is optically inactive.
(ii) The presence of nitro group ($-NO_2$) at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. *(Delhi 2015)*

OR

Write the structures and names of the compounds formed when compound '*A*' with molecular formula, C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

26. Account for the following :
(i) Phenols do not give protonation reactions readily.
(ii) Alcohols act as Bronsted acid and Bronsted base both.

OR

Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols. Give reason.

27. Write a chemical test to distinguish between :
(i) Chlorobenzene and benzyl chloride
(ii) Chloroform and carbon tetrachloride

SECTION - C

28. Compound '*A*' with molecular formula C_4H_9Br is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound '*A*' only. When an optically active isomer '*B*' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be

dependent on concentration of compound 'B' and KOH both.

(i) Write down the structural formula of both compounds '*A*' and '*B*'.

(ii) Out of these two compounds, which one will be converted to the product with inverted configuration?

29. (i) What happens when phenol is treated with bromine water?

(ii) Write the equation involved in the following reactions :

(a) Kolbe's reaction

(b) Reimer–Tiemann reaction

OR

What happens when

(i) ethyl alcohol reacts with red P and Br_2?

(ii) anisole is treated with Br_2 in CH_3COOH?

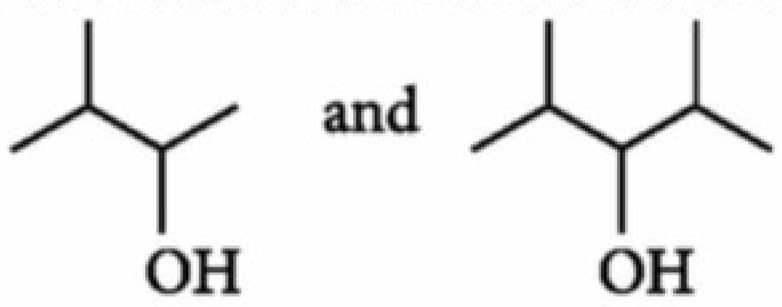
(iii) 3°alcohol is treated with $KMnO_4$ at high temperature?

30. (i) Is it desirable to synthesise alcohols in a copper vessel?

(ii) Draw the structures of all the isomeric alcohols of molecular formula $C_5H_{12}O$, give their IUPAC names. Classify them as 1°, 2° and 3° alcohols.

31. A sweet smelling organic compound '*A*' is slowly oxidised by air in the presence of light to a highly poisonous gas. On warming with silver powder it forms a gaseous substance '*B*' which is also produced by the action of calcium carbide on water. Identify '*A*' and '*B*' and write the equations of the reactions involved.

32. (a) Identify the chiral molecule in the following pair :



(i) (ii)

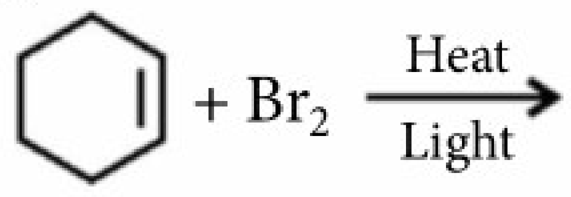
(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. ***(2018)***

OR

(a) A chloro derivative (*A*) on treatment with zinc-copper couple gives a hydrocarbon with five carbon atoms. When (*A*) is dissolved in ether and treated with sodium then 2, 2, 5, 5-tetramethylhexane is obtained. What is the original compound (*A*)?

(b) Draw the structure of major monohalogen product in the following reaction :



33. (a) Give chemical tests to distinguish between the following pairs of compounds :

(i) Pentan-2-ol and pentan-3-ol

(ii) Ethanol and phenol

(b) *o*-Nitrophenol is more acidic than *o*-methoxyphenol. Explain why.

34. How would you convert the following :

(i) Phenol to benzoquinone

(ii) Propanone to 2-methylpropan-2-ol

(iii) Propene to propan-2-ol

SECTION - D

35. (a) Phenol is acidic while hexanol is neutral towards a solution of NaOH. Why?

(b) *m*-Aminophenol is stronger acid than *o*-aminophenol. Explain.

(c) Name the different reagents needed to perform the following reactions :

(i) Phenol to benzene

(ii) Friedel-Crafts alkylation of anisole

(iii) Dehydrogenation of ethanol to ethanal

OR

(i) Write the structure of the products when butan-2-ol reacts with the following :

(a) CrO_3 **(b)** $SOCl_2$

(ii) How is 1-propoxypropane synthesised from propan-1-ol ? Give mechanism.

36. (a) The following reaction proceeds by an S_N2 pathway :

$$C_6H_5CH_2Br + NaN_3 \longrightarrow C_6H_5CH_2N_3 + NaBr$$

(i) Write an equation for the expected rate constant.

(ii) Draw a potential energy diagram for the reaction.

(iii) How would the rate of the reaction change if concentration of sodium azide is doubled ?

(b) Write the mechanism of the following reaction :

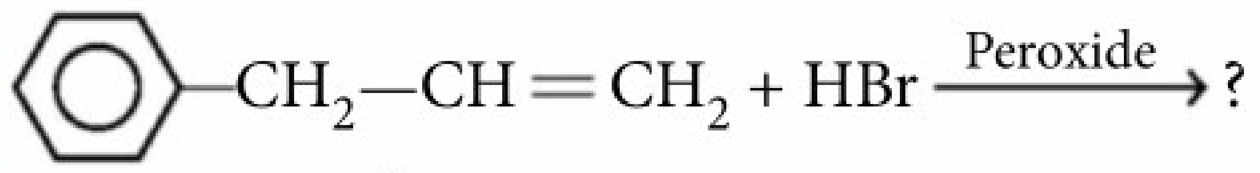
$$n\text{-BuBr} + KCN \xrightarrow{EtOH,\ H_2O} n\text{-BuCN}$$

OR

Complete the following reactions :

(a) $CH_3CH_2COOAg \xrightarrow{Br_2} ? \xrightarrow{alc.\ KOH} ?$

(b) $CH_3CH_2CH_2Cl \xrightarrow{CH_3C\equiv CNa} ?$

(c) 

(d) $CH_3\underset{\underset{CH_3}{|}}{C}HI \xrightarrow[\text{Dry ether}]{Na} ?$

(e) $CH_3CH{=}CH_2 \xrightarrow{HBr} ? \xrightarrow{aq.\ KOH} ?$

37. **(a)** Phenols are stronger acids than alcohols, why?

(b) Draw resonance structures of phenol and phenoxide ion.

(c) What is aspirin? How is aspirin prepared?

OR

(a) How do you convert the following :

(i) Phenol to anisole

(ii) Ethanol to propan-2-ol

(b) Write mechanism of the following reaction :

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

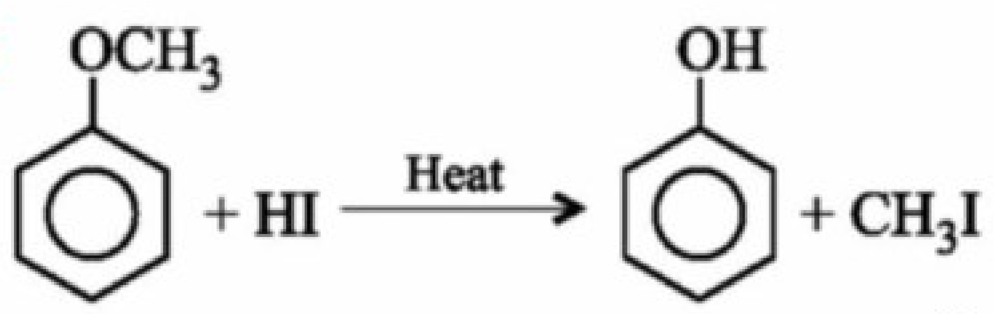
(c) Why phenol undergoes electrophilic substitution more easily than benzene? ***(Delhi 2019)***

SOLUTIONS

1. **(b)** **2.** **(b)**

3. **(b) :** Greater is the electron density on aromatic ring, greater is the reactivity towards electrophilic aromatic substitution.

4. **(a) :**



5. **(c) :** $CH_3CH(OH)CH_2CH_3 \xrightarrow{[O]} CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$

2-Butanol Ethyl methyl ketone

6. **(d) :** The reason for the lesser volatility of alcohols than ethers is the intermolecular association of a large number of alcohol molecules due to hydrogen bonding as —OH group is highly polarised.

No such hydrogen bonding is present in ethers.

7. **(a)**

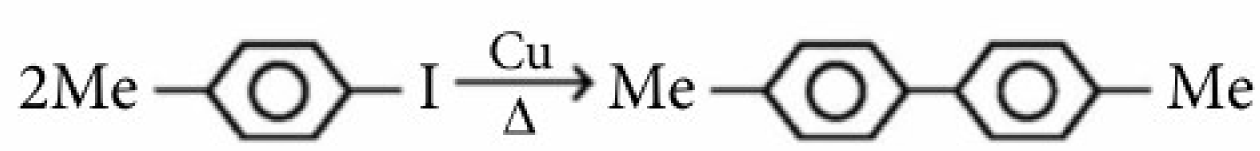
8. **(a) :** $CHCl_3 + HNO_3 \longrightarrow CCl_3NO_2 + H_2O$

Chloropicrin

9. **(b)** **10.** **(c)**

11. Order of increasing S_N2 reactivity :

$CH_3Br > CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl$

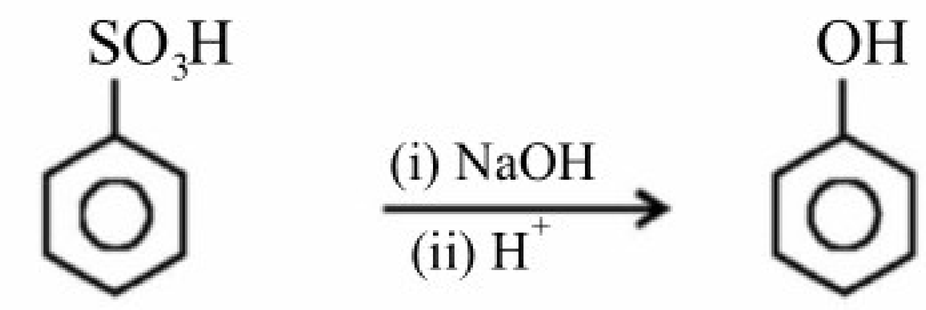
12. 

13. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H–bond among water molecules is much higher than energy released by water halide interaction.

14. $CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3{-}CH_2{-}CH_2OH$

Propene Propan-1-ol

15. When benzene sulphonic acid is fused with NaOH, sodium phenoxide is formed which on hydrolysis yields phenol.



Benzene sulphonic acid Phenol

16. 2-Methylprop-2-en-1-ol

17. $CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Br + Na^+\bar{O}{-}CH_3 \longrightarrow$

t-Butyl bromide

$CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 + NaBr + CH_3OH$

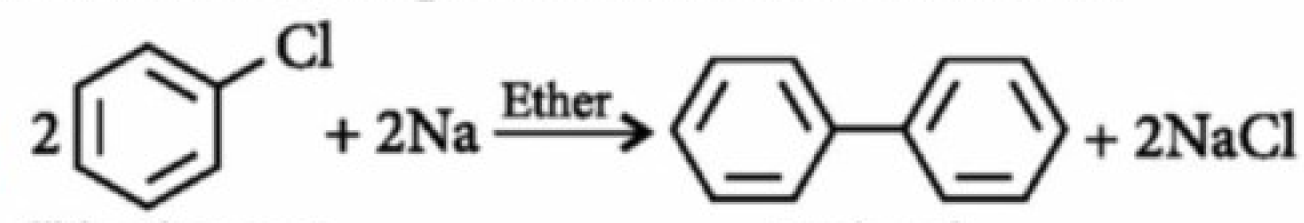
2-Methylpropene

18. 3° > 2° > 1° (order of dehydration of alcohol)

19. $\bar{C}Cl_3$ obtained by the removal of proton from $CHCl_3$ is stabilized by resonance due to the presence of *d*-orbitals in chlorine while $\bar{C}F_3$ is not stabilized by resonance due to absence of *d* -orbitals in fluorine.

20. Order of increasing boiling points of alkyl halides :
$R-I > R-Br > R-Cl > R-F$

21. In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring.
C — Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore they are less reactive towards nucleophilic substitution reaction.

22. **(i)** 

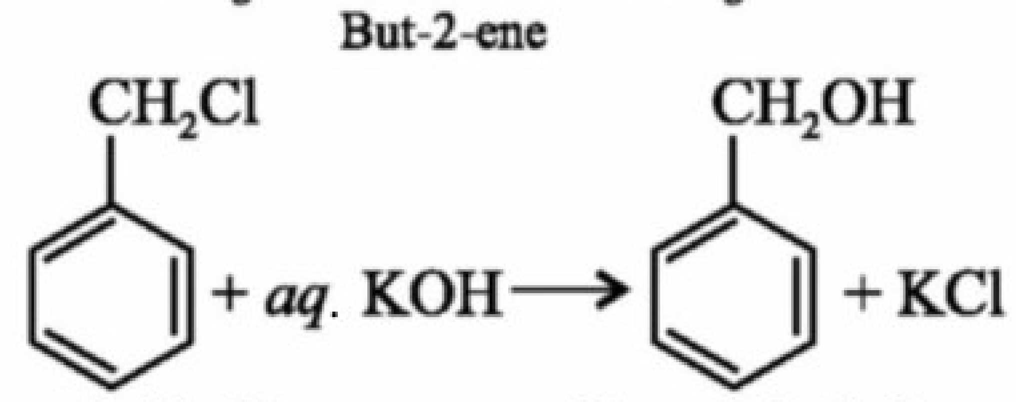
Chlorobenzene Biphenyl

(ii) $CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CH_2{-}CH_3 \xrightarrow[\Delta]{\text{ethanolic KOH}}$

2-Bromobutane

$CH_3{-}CH{=}CH{-}CH_3 + KBr + H_2O$

But-2-ene

23. **(i)** 

Benzyl chloride Benzyl alcohol

(ii) $CH_3CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br$
Propene

$\xrightarrow[\text{Acetone}]{\text{NaI}} CH_3-CH_2-CH_2I$
1-Iodopropane

24. Methanol is manufactured by catalytic hydrogenation of carbon monoxide at high pressure and temperature.

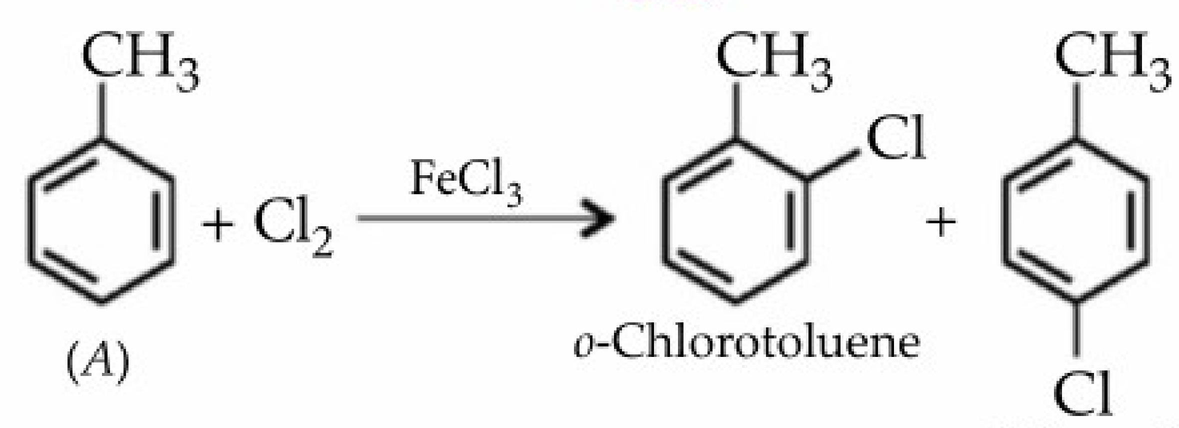
$CO + 2H_2 \xrightarrow[\text{200-300 atm}]{ZnO-Cr_2O_3} CH_3OH$

Methanol is chiefly used for the preparation of formaldehyde.

25. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.

(ii) The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

OR



(*A*) *o*-Chlorotoluene *p*-Chlorotoluene

26. (i) Due to electron withdrawing effect of phenyl group, the electron density on the oxygen atom of –OH group in phenol is less. Hence phenols do not undergo protonation.

(ii) Due to presence of lone pair of electrons on oxygen atom, alcohols accept a proton which makes them Bronsted base and due to acidic hydrogen they donate the proton to strong base which makes them Bronsted acid.

OR

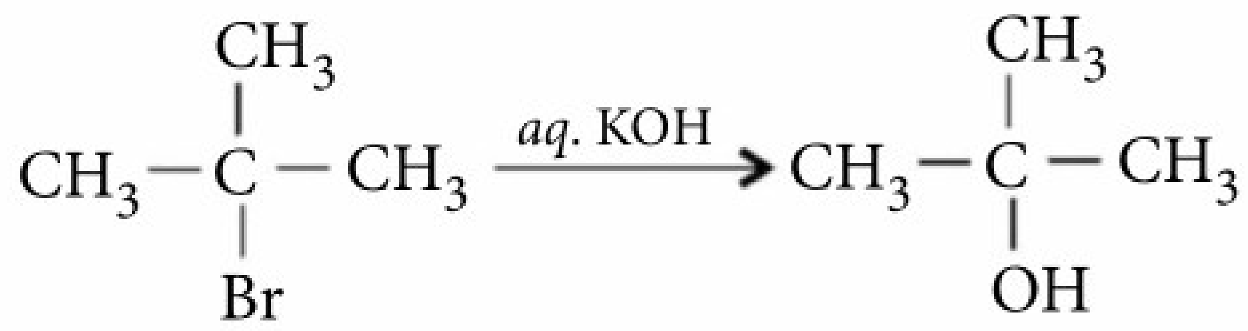
The order of reactivity of alcohols with sodium metal is of the order : Primary > Secondary > Tertiary.

Electron releasing inductive effect of alkyl group in alcohols increases the electron density around O–H bond which makes the O–H bond stronger and makes the alcohol a weaker acid. Therefore more the number of alkyl groups, stronger is the O–H bond and weaker acid is the alcohol.

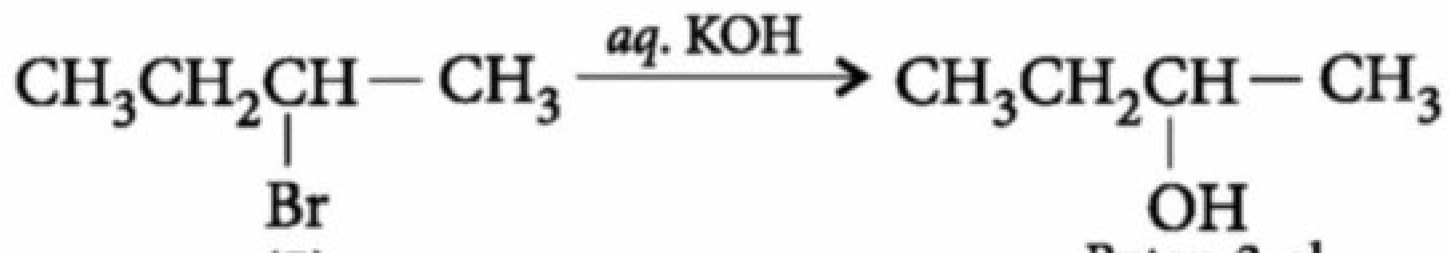
27. (i) Benzyl chloride gives white precipitate with $AgNO_3$ solution while chlorobenzene does not.

(ii) $CHCl_3$ with aniline in presence of alc. KOH gives foul smelling isocyanides whereas CCl_4 does not.

28. (i)



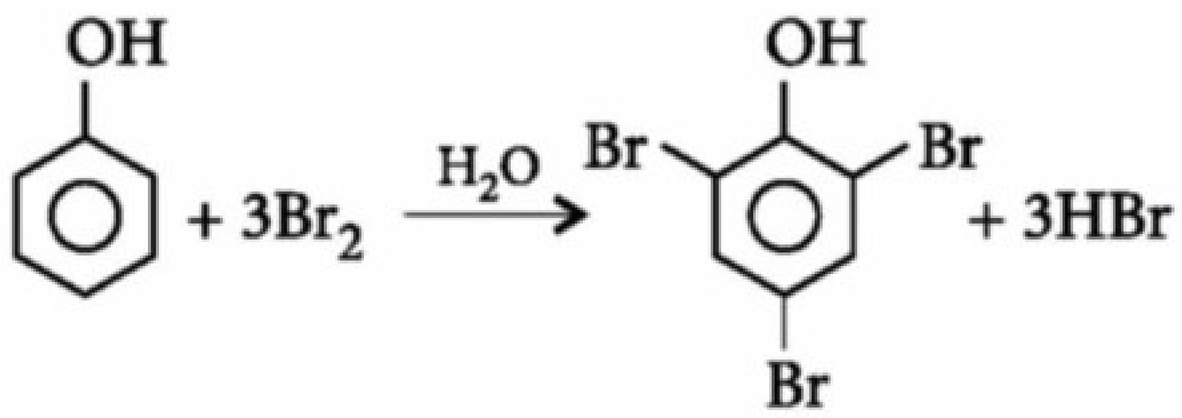
(*A*) 2-Bromo-2-methylpropane 2-Methylpropan-2-ol



(*B*) 2-Bromobutane (Optically active) Butan-2-ol

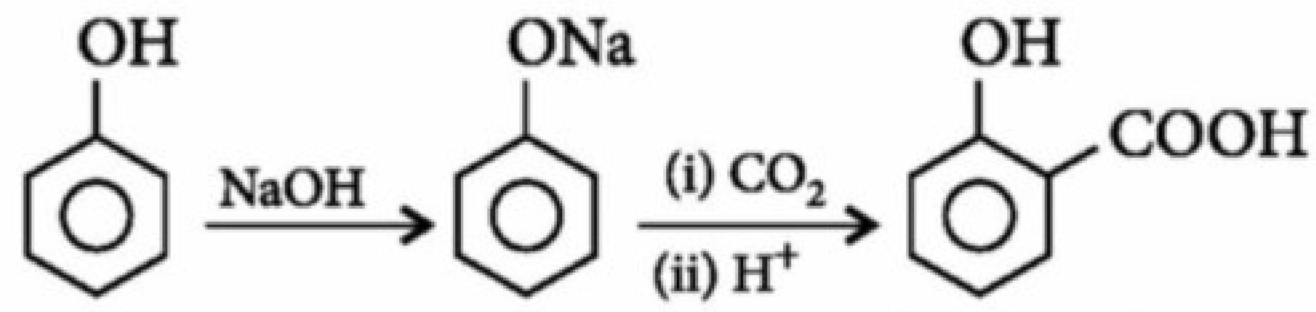
(ii) Compound (*B*) will be converted to product with inverted configuration as it undergoes S_N2 nucleophilic substitution. Compound (*A*) being a tertiary halide, undergoes S_N1 substitution which is accompanied by racemisation.

29. (i) When phenol is treated with bromine water, 2, 4, 6-tribromophenol is formed.



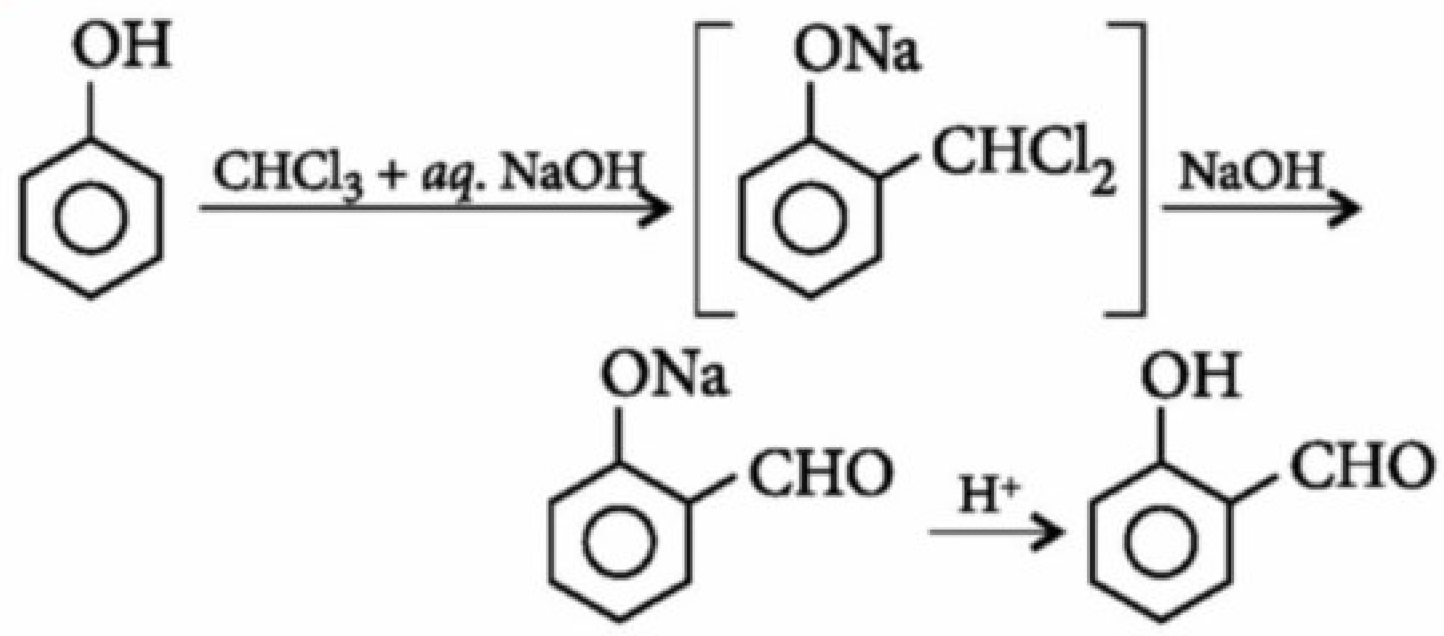
2, 4, 6-Tribromophenol

(ii) (a) Kolbe's reaction :



Salicylic acid

(b) Reimer–Tiemann reaction :



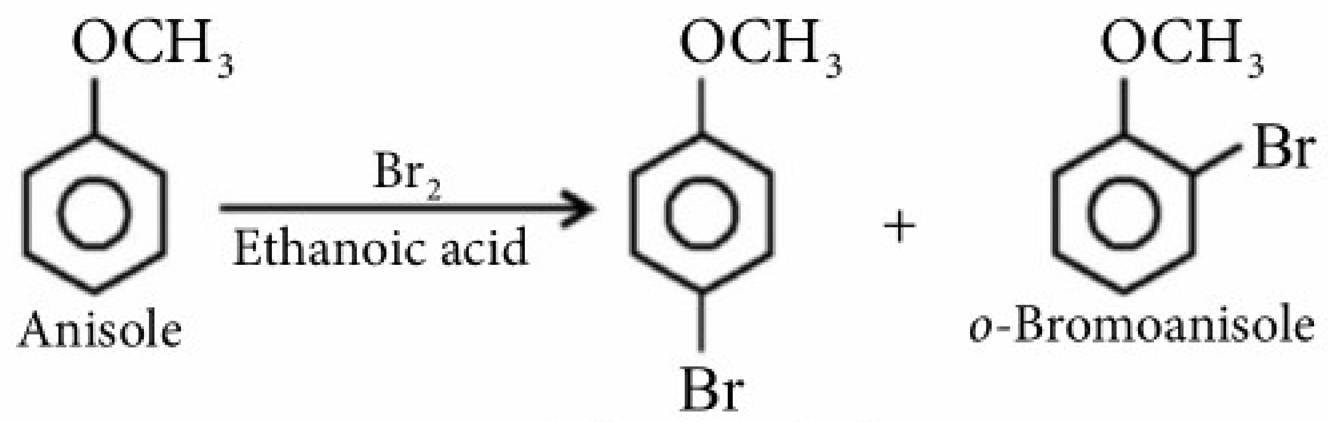
Salicylaldehyde

OR

(i) Ethyl alcohol on reaction with red P and Br_2 gives ethyl bromide.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{\text{Red P} + Br_2} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_3PO_3$$

(ii) Anisole on treatment with bromine in acetic acid produces a mixture of *p*-bromoanisole and *o*-bromoanisole.



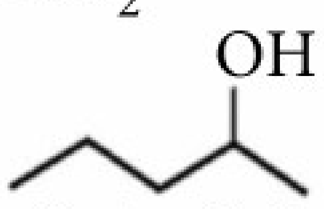
(iii) 3° alcohol reacts with $KMnO_4$ at high temperature to give carboxylic acid having lesser number of carbon atoms.

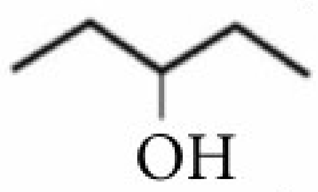
$$\underset{\text{2-Methylbutan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_3} \xrightarrow{KMnO_4} \underset{\text{Propanone}}{\overset{CH_3}{\underset{CH_3}{>}}C=O} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

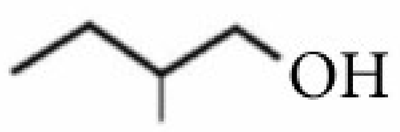
30. (i) It is not desirable to synthesise alcohols in copper vessel as it can undergo oxidation or dehydration.

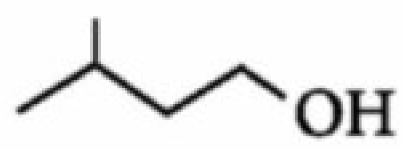
$$CH_3CH_2OH \xrightarrow{Cu,\ \Delta} CH_3CHO$$
$$(CH_3)_2CHOH \xrightarrow{Cu,\ \Delta} (CH_3)_2C=O$$
$$(CH_3)_3COH \xrightarrow{Cu,\ \Delta} (CH_3)_2C=CH_2$$

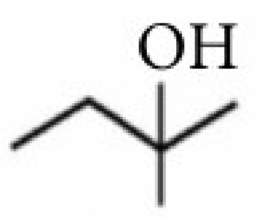
(ii) (a) 
Pentan-1-ol
(1°)

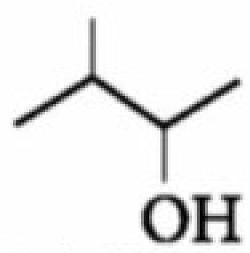
(b) 
Pentan-2-ol
(2°)

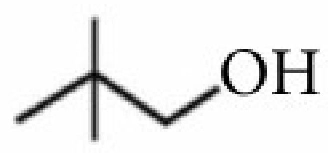
(c) 
Pentan-3-ol
(2°)

(d) 
2-Methylbutan-1-ol
(1°)

(e) 
3-Methylbutan-1-ol
(1°)

(f) 
2-Methylbutan-2-ol
(3°)

(g) 
3-Methylbutan-2-ol
(2°)

(h) 
2, 2-Dimethylpropan-1-ol
(1°)

31. The sweet smelling organic compound '*A*' is chloroform ($CHCl_3$). Its chemical reactions are as follows :

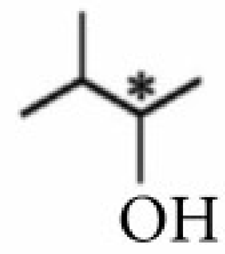
$$\underset{\substack{\text{Chloroform}\\(A)}}{CHCl_3} + \underset{\text{Air}}{1/2\ O_2} \xrightarrow{\text{Light}} \underset{\text{Phosgene}}{COCl_2} + HCl$$

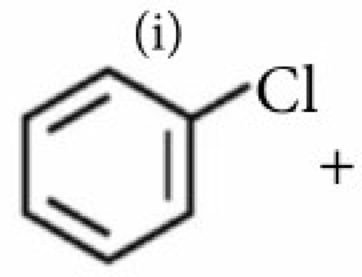
Phosgene is a highly poisonous gas. The action of chloroform with silver powder gives acetylene (*B*).

$$2\ CHCl_3 + 6Ag \xrightarrow{\text{Heat}} \underset{\substack{\text{Acetylene}\\(B)}}{CH\equiv CH} + 6AgCl$$

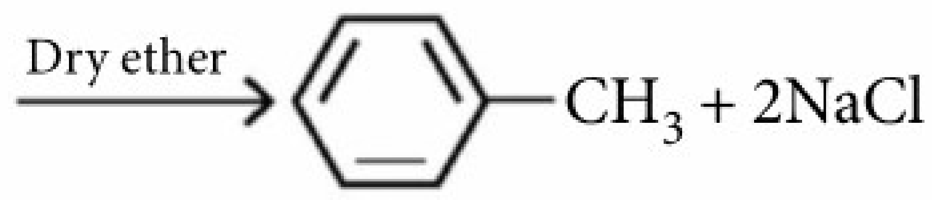
Calcium carbide when reacted with water also gives acetylene.

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{CH\equiv CH}$$

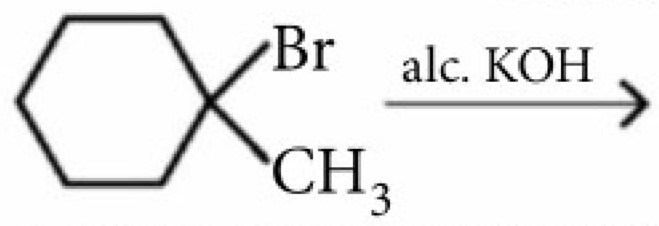
32. (a) 
(i)

(b) 

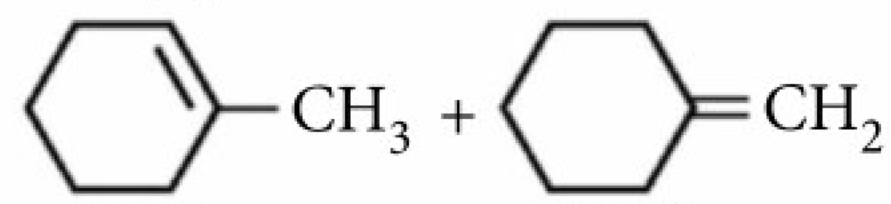
Chlorobenzene
$+ 2Na + \underset{\text{Methyl chloride}}{Cl-CH_3}$



Toluene

(c) 

1-Bromo-1-methylcyclohexane



(major) (minor)

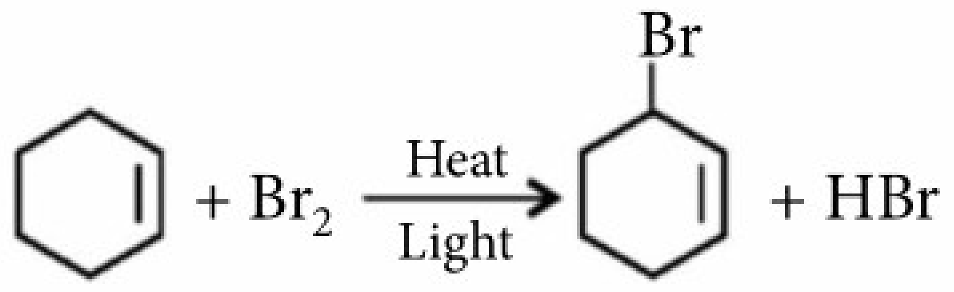
OR

(a)
$$\underset{(A)}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl} \xrightarrow[\text{reduction}]{\text{Zn-Cu}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$\downarrow \text{Na, ether (Wurtz reaction)}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2, 2, 5, 5-tetramethyl hexane

(b) 

33. (a) (i) On adding I_2 and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.

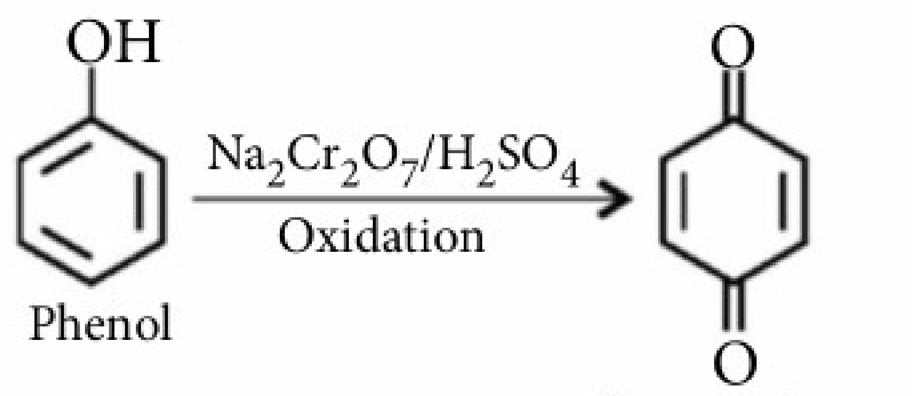
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_2CH_3 \xrightarrow{I_2 + NaOH} \underset{\text{Yellow ppt.}}{CHI_3} + CH_3CH_2CH_2COONa$$

(ii) Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + FeCl_3 \longrightarrow \textbf{No violet colouration}$$

(b) Electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group is an electron donating group. Methoxy group destabilises the phenoxide ion by intensifying the negative charge. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

34. (i) 

Phenol → Benzoquinone

(ii)
$$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_3 + CH_3MgBr \longrightarrow \left[CH_3-\overset{\displaystyle OMgBr}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3\right] \xrightarrow{H_2O} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3}$$

(iii)
$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[H_2O]{H_2SO_4} \underset{\textbf{Propan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_3}$$

35. (a) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus, phenol loses H^+ ion to show acidic character.

$$C_6H_5OH \longrightarrow \underset{\text{Resonance stabilised}}{C_6H_5O^-} + H^+$$

On the other hand, alkoxide ion formed from hexanol shows no such resonance stabilisation and is unstable.

(b) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus *m*-aminophenol is stronger acid than *o*-aminophenol.

(c) (i) Zinc dust

(ii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_3$ (anhy.)

(iii) Cu/573 K

OR

(i)

(a)
$$\underset{\text{Butan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2-CH_3} \xrightarrow{CrO_3} \underset{\text{Butan-2-one}}{CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_2CH_3}$$

(b)
$$\underset{\text{Butan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2-CH_3} \xrightarrow{SOCl_2} \underset{\text{2-Chlorobutane}}{CH_3-\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_2-CH_3}$$

(ii) Propan-1-ol on treatment with conc. H_2SO_4 at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.

$$\underset{\text{Propan-1-ol}}{2CH_3-CH_2-CH_2-OH} + H_2SO_4 \xrightarrow{413\ K} \underset{\text{1-Propoxypropane}}{CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3}$$

Mechanism :

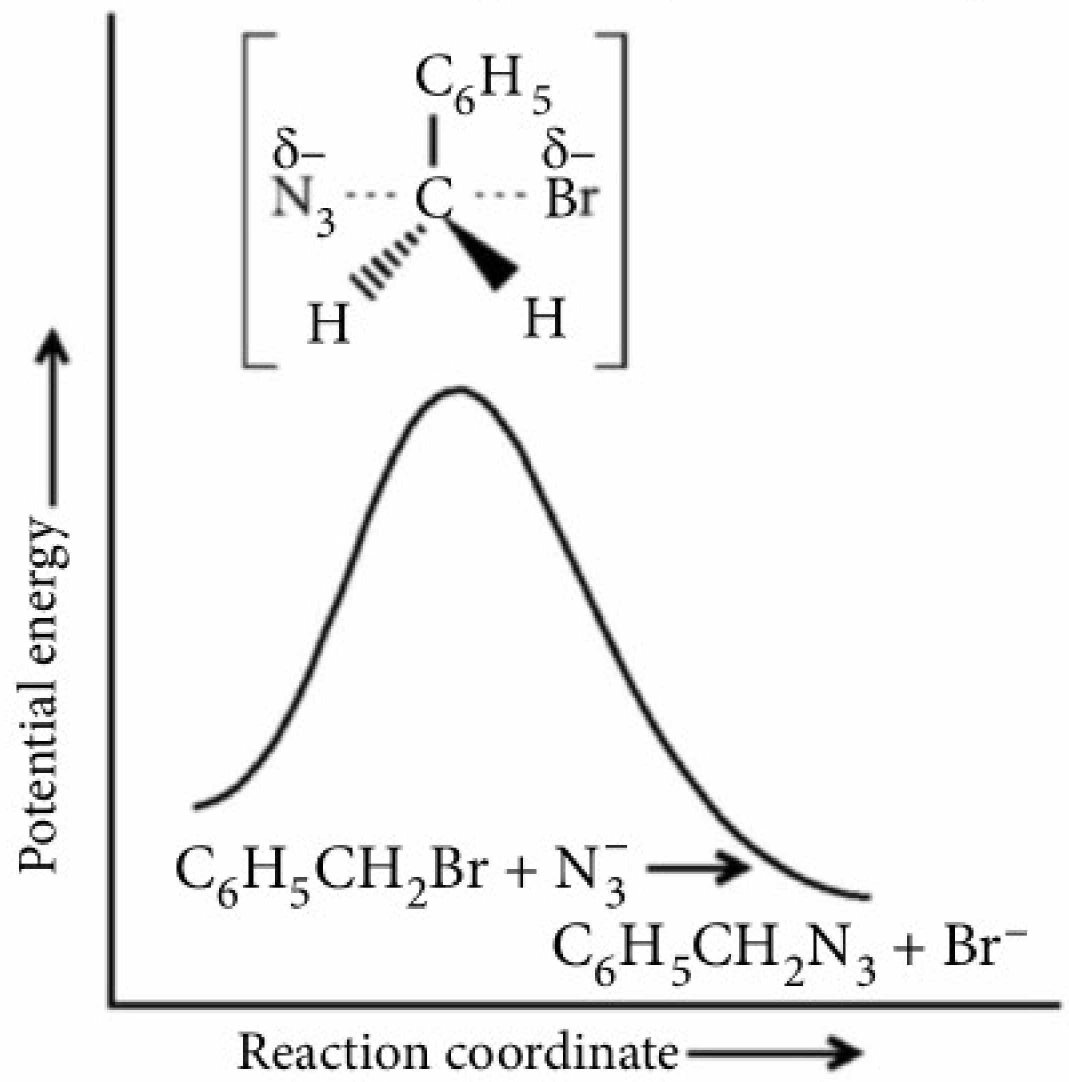
$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} + H^+ \rightleftharpoons CH_3-CH_2-CH_2-\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}-H$$

$$CH_3-CH_2-CH_2-\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}-H \rightleftharpoons CH_3-CH_2-\overset{+}{C}H_2 + H_2O$$

$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H} + CH_3-CH_2-\overset{+}{C}H_2 \xrightarrow{-H^+} CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$$

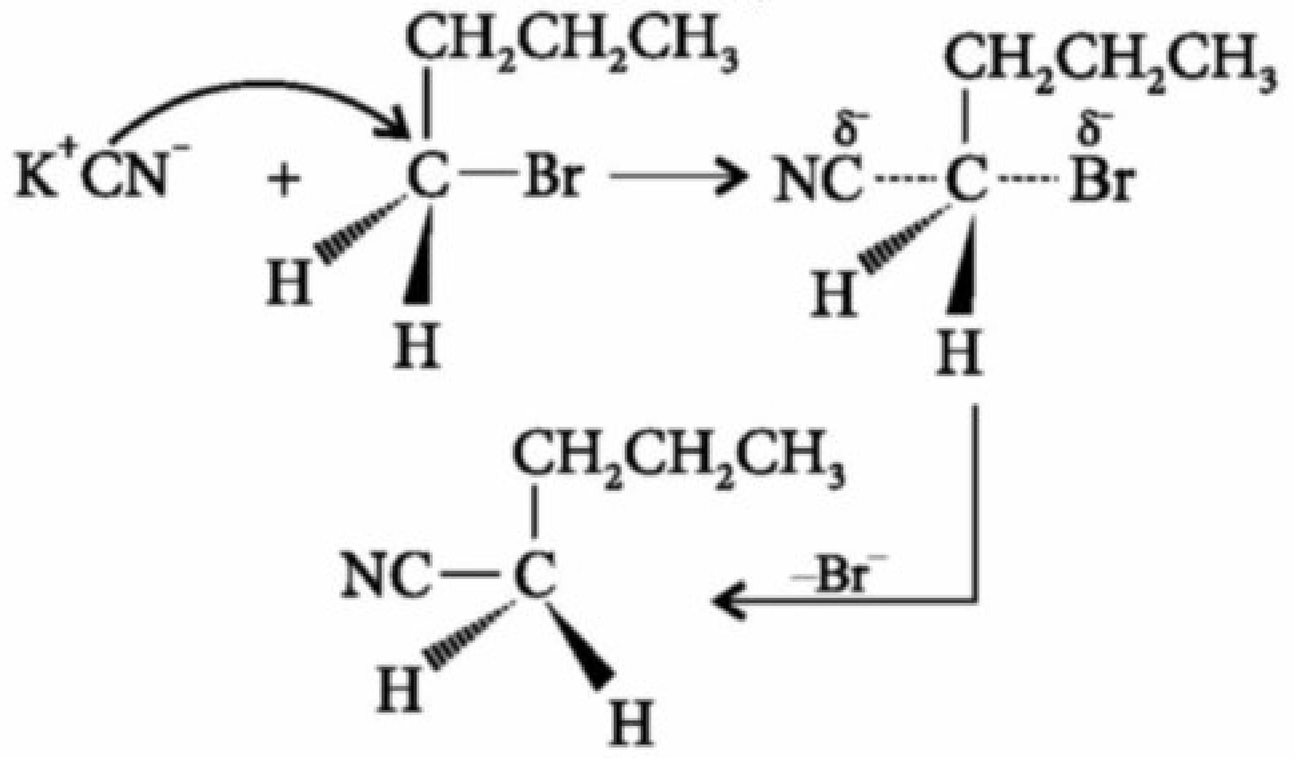
36. (a) (i) Rate = $k[C_6H_5CH_2Br]\,[NaN_3]$

(ii)



(iii) The rate will be doubled.

(b) *n*-butyl bromide will give S_N2 reaction :



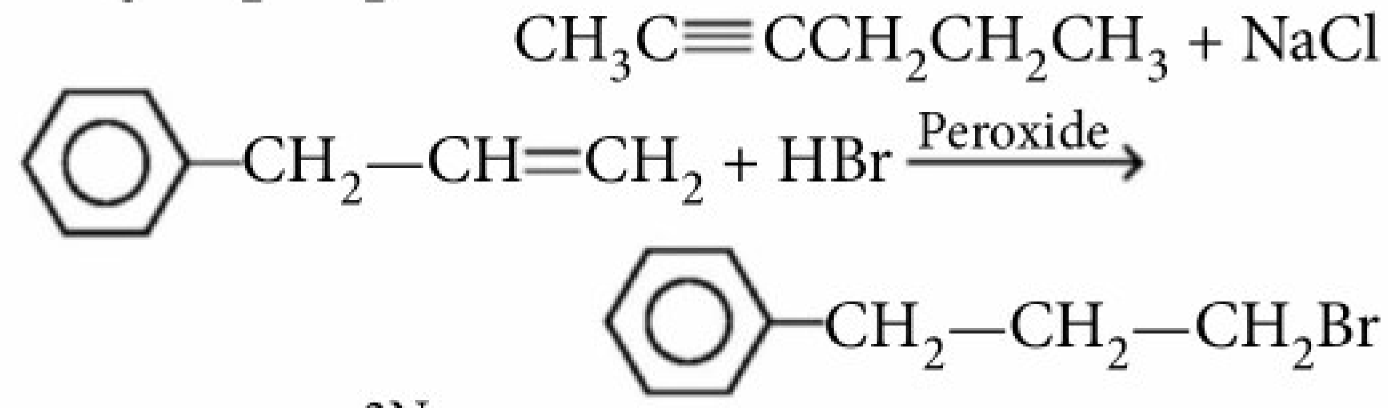
n-Butyl cyanide

OR

(a) $CH_3CH_2COOAg \xrightarrow{Br_2} CH_3CH_2Br \xrightarrow{\text{alc. KOH}} CH_2{=}CH_2$

(b) $CH_3CH_2CH_2Cl \xrightarrow{CH_3C\equiv CNa} CH_3C\equiv CCH_2CH_2CH_3 + NaCl$

(c)

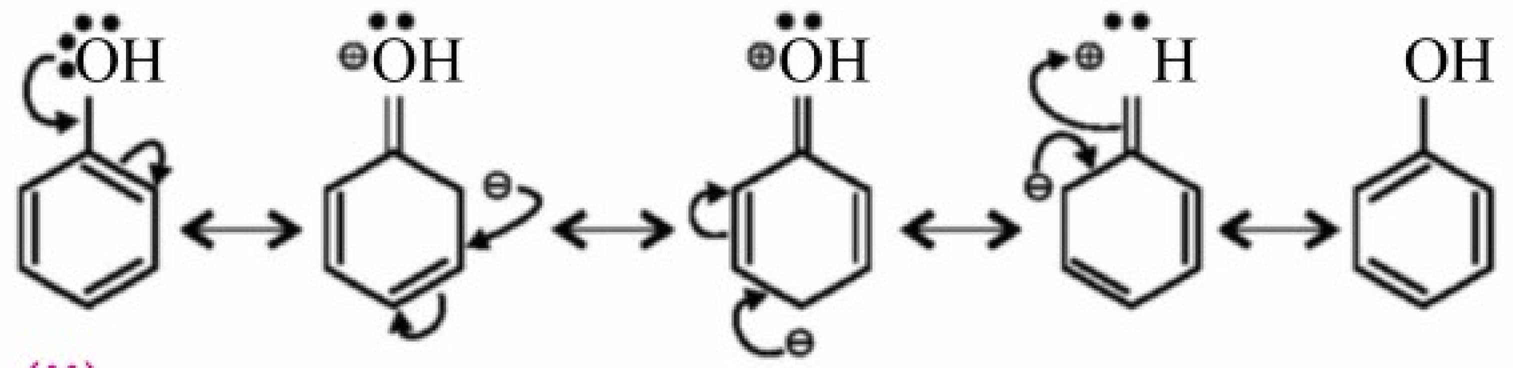


(d) $2CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HI \xrightarrow[\text{Dry ether}]{2Na} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3 + 2NaI$

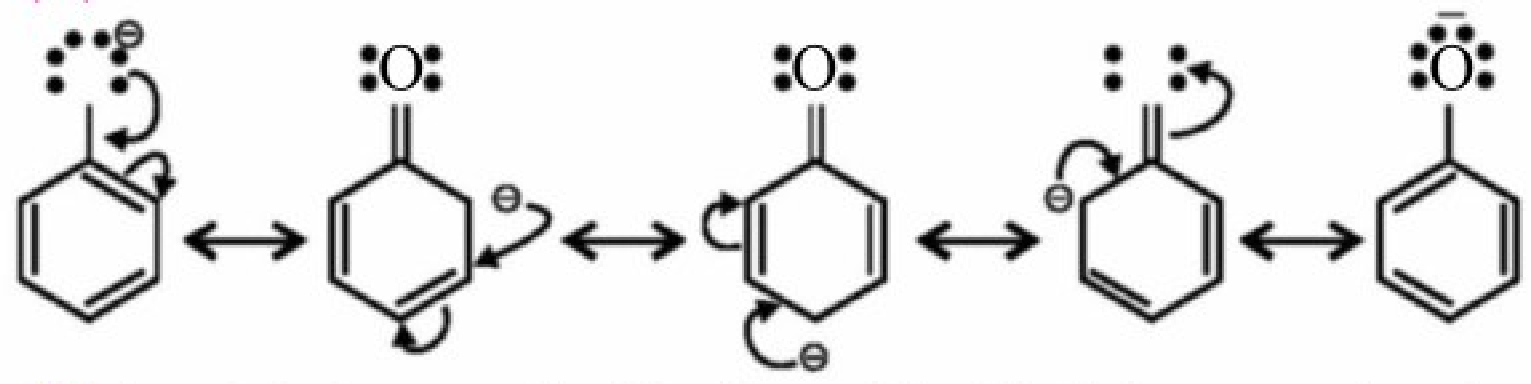
(e) $CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}CH_3 \xrightarrow{\text{aq. KOH}} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3$

37. (a) In alcohols, –OH group is attached to electron releasing alkyl group which decreases polarity of O – H bond while in phenols –OH group is attached to electron withdrawing phenyl group which increases polarity of O – H bond.

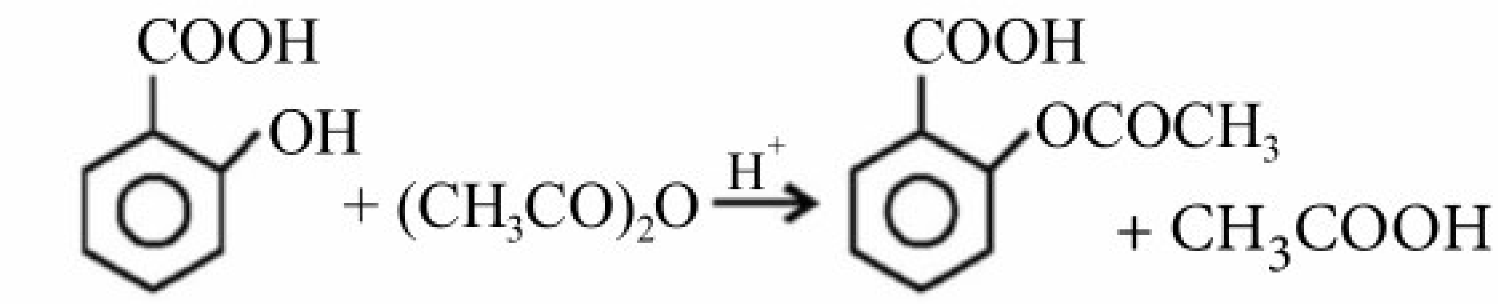
(b) (i)



(ii)



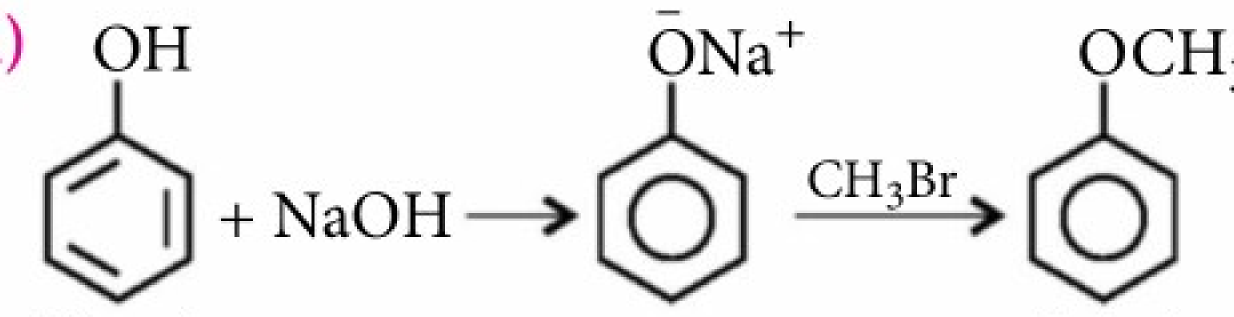
(c) Aspirin is acetyl salicylic acid which is an analgesic used in pain relieving.



Salicylic acid — Acetyl salicylic acid (Aspirin)

OR

(a) (i)

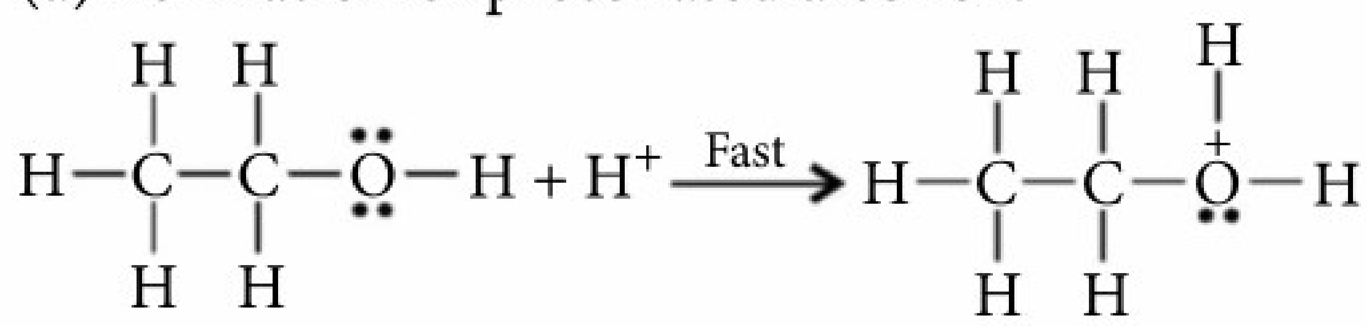


Phenol — Anisole

(ii) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCC} CH_3CHO \xrightarrow[H_2O]{CH_3MgBr} \underset{\text{Propan-2-ol}}{CH_3\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_3}$

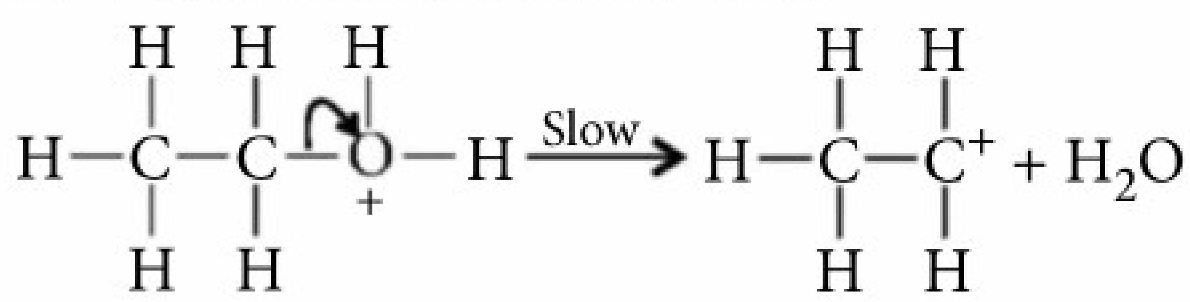
(b) Mechanism : The dehydration of ethanol involves the following steps :

(a) Formation of protonated alcohol :

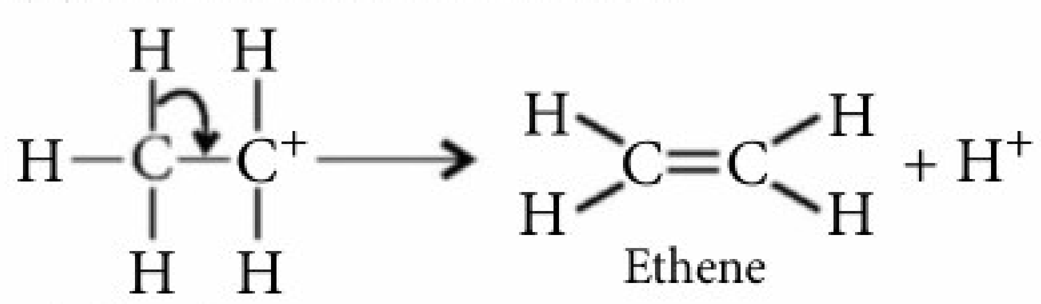


Protonated alcohol

(b) Formation of carbocation :



(c) Formation of ethene :



Ethyl carbocation — Ethene

(c) Phenols undergo electrophilic substitution reaction more easily than benzene due to strong activating effect of –OH group attached to benzene ring.

MONTHLY TEST DRIVE

XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

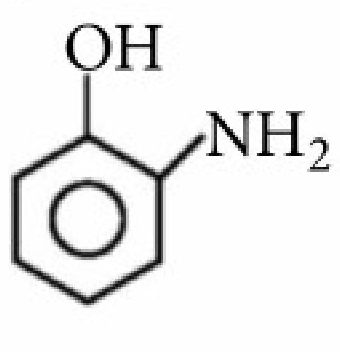
Total Marks : 120 **BIOMOLECULES | POLYMERS | CHEMISTRY IN EVERYDAY LIFE** **Time Taken : 60 Min.**

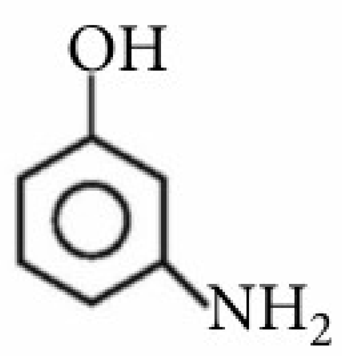
NEET / AIIMS

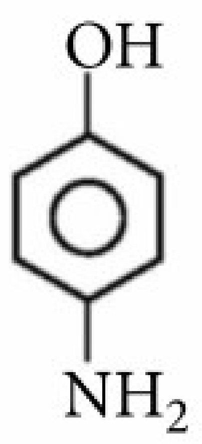
Only One Option Correct Type

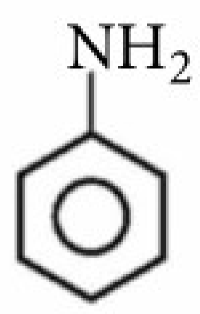
1. Which of the following hexoses will form the same osazone when treated with excess of phenylhydrazine?
   (a) D-glucose, D-fructose and D-galactose
   (b) D-glucose, D-fructose and D-mannose
   (c) D-glucose, D-mannose and D- galactose
   (d) D-fructose, D-mannose and D-galactose

2. Which of the following gives paracetamol on acetylation?

(a) 

(b) 

(c) 

(d) 

3. Novolac, the linear polymer used in paints is
   (a) copolymer of 1, 3-butadiene and styrene
   (b) obtained by the polymerization of methyl methacrylate
   (c) initial product obtained in the condensation of phenol and formaldehyde in the presence of acid or base catalyst
   (d) obtained by the polymerization of caprolactam

4. Polyvinyl alcohol can be prepared by
   (a) polymerisation of vinyl alcohol
   (b) alkaline hydrolysis of polyvinyl acetate
   (c) polymerisation of acetylene
   (d) reaction of acetylene with H_2SO_4 in presence of $HgSO_4$.

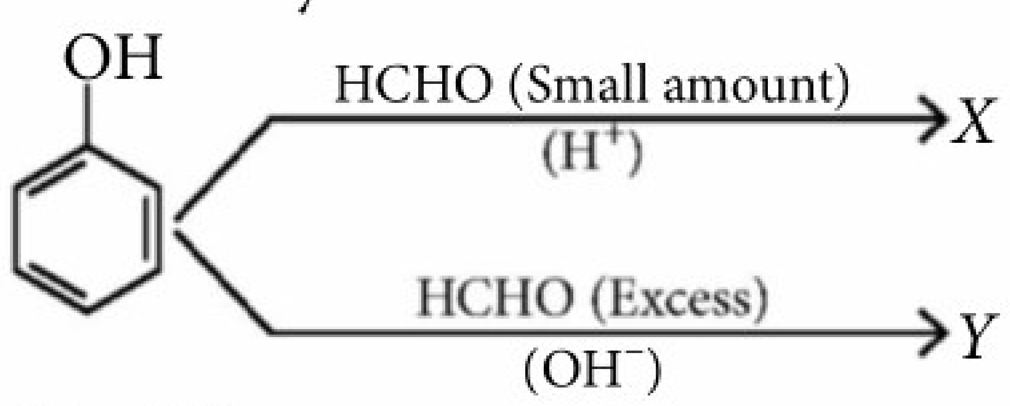
5. The reagent which may be used to distinguish between cane sugar and glucose solution is
   (a) Molisch's reagent (b) iodine solution
   (c) Baeyer's reagent (d) Fehling's solution.

6. Sodium metabisulphite is used in preserving squashes and other mildly acidic foods because
   (a) potassium salt has preservative action
   (b) sulphur dioxide and sulphurous acid formed kill bacteria and germs
   (c) potassium metabisulphite prevents oxidation
   (d) potassium metabisulphite is not influenced by acid.

7. In both DNA and RNA, heterocyclic base and phosphate ester linkages are at
   (a) C-5′ and C-2′ respectively of the sugar molecule
   (b) C-2′ and C-5′ respectively of the sugar molecule
   (c) C-1′ and C-5′ respectively of the sugar molecule
   (d) C-5′ and C-1′ respectively of the sugar molecule.

8. Which of the following alkenes is most reactive towards cationic polymerization?
   (a) $CH_2{=}CHCH_3$ (b) $H_2C{=}CHCl$
   (c) $H_2C{=}CHC_6H_5$ (d) $H_2C{=}CHCO_2CH_3$

9. Phenol gives two polymers on condensation with formaldehyde:



   X and *Y* are

	X	***Y***
(a)	bakelite	novolac
(b)	novolac	bakelite
(c)	bakelite	bakelite
(d)	novolac	novolac.

10. Pick out the statement which is not true?
   (a) Tetrazine is harmful edible colour.
   (b) Alitame is an artificial sweetener.
   (c) Sodium alkyl sulphate is a cationic detergent.
   (d) BHT is an antioxidant.

11. Cheilosis and digestive disorders are due to the deficiency of
   (a) ascorbic acid (b) pyridoxine
   (c) thiamine (d) riboflavin.

12. The role of phosphate in detergent powder is to
   (a) control pH level of the detergent water mixture
   (b) remove Ca^{2+} and Mg^{2+} ions from the water that cause the hardness of water
   (c) provide whiteness to the fabrics
   (d) form solid detergents as phosphateless detergents are liquid in nature.

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** Alpha (α–) amino acids exist as internal salt in solution as they have amino and carboxylic acid groups in near vicinity.
   Reason : H^+ ion given by carboxylic (–COOH) group is captured by amino ($-NH_2$) group having lone pair of electrons.

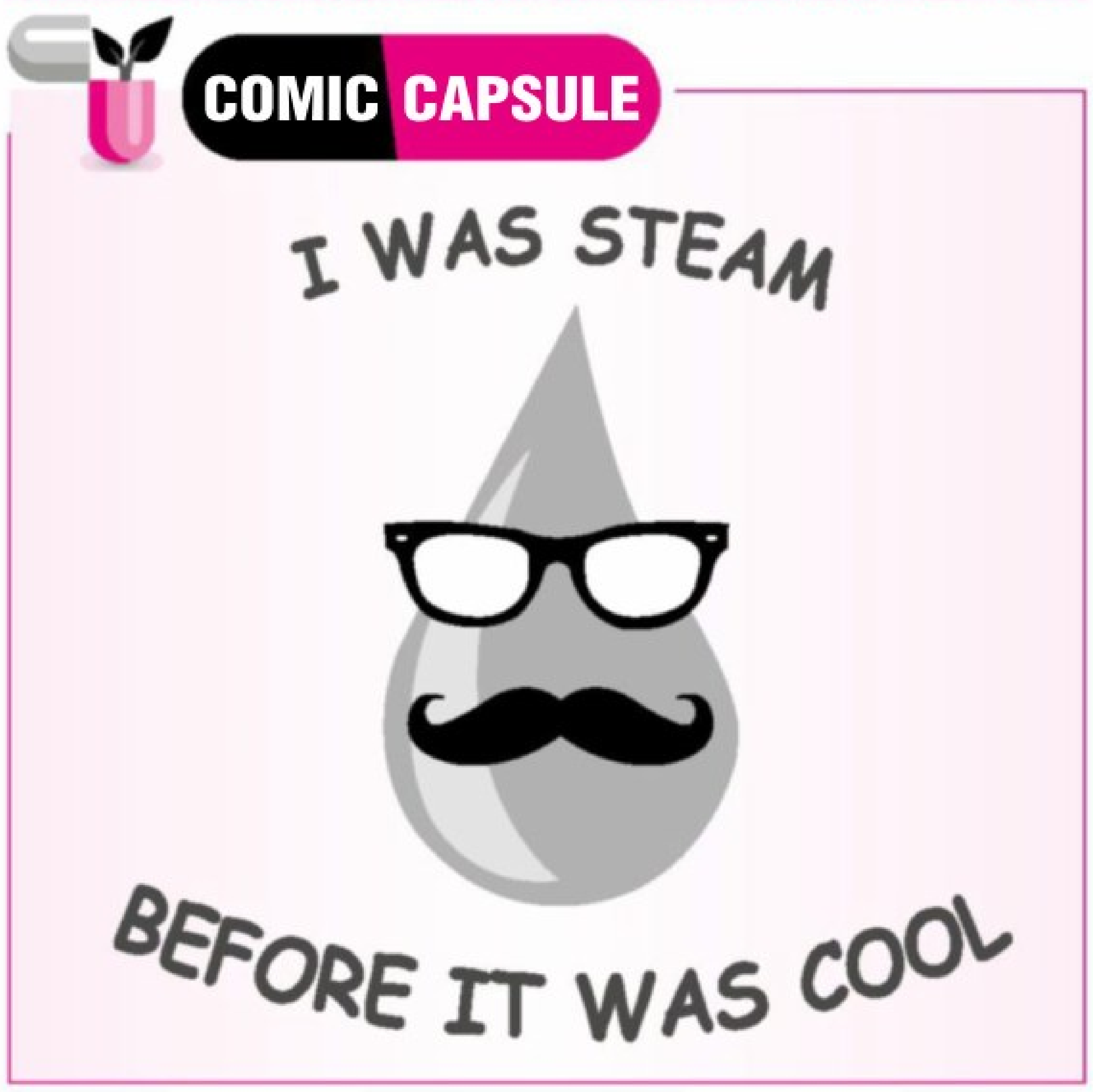
14. **Assertion :** Polyamides are best used as fibres because of high tensile strength.
   Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

15. **Assertion :** The —As=As— linkage present in arsphenamine (a sulpha drug) resembles the —N=N— linkage present in azo dyes.
   Reason : The first antibacterial agent, prontosil resembles in structure to the compound salvarsan.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. The most important contribution to the stability of a protein conformation appears to be the
   (a) entropy increase from the decrease in ordered water molecules forming a solvent shell around it



(b) maximum entropy increase from ionic interactions between the ionized amino acids in a protein
(c) sum of free energies of formation of many weak interactions between its polar amino acids and surrounding water molecules
(d) sum of free energies of formation of many weak interactions among the hundreds of amino acids in a protein.

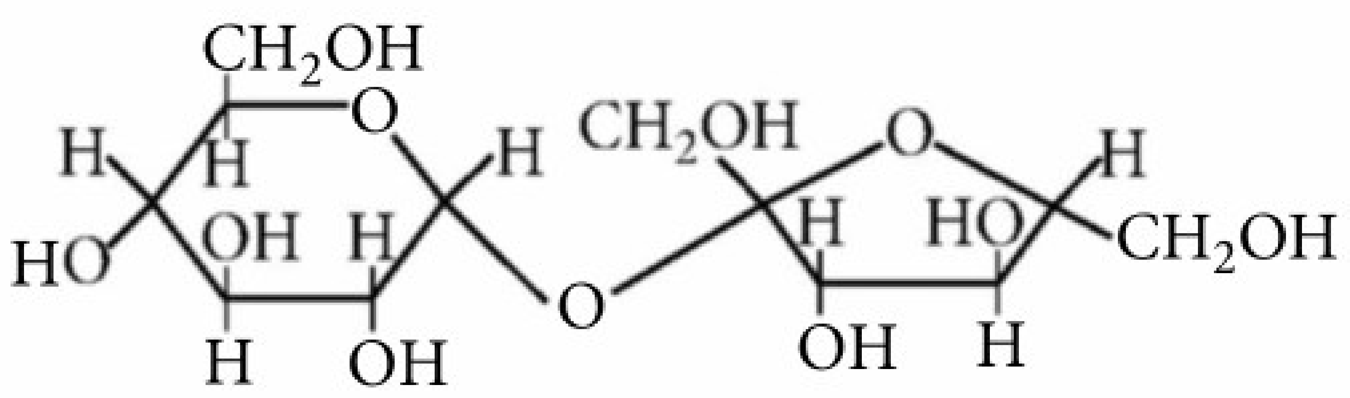
17. Antiseptic chloroxylenol is
(a) 4-chloro-3, 5-dimethylphenol
(b) 3-chloro-4, 5-dimethylphenol
(c) 4-chloro-2, 5-dimethylphenol
(d) 5-chloro-3, 4-dimethylphenol

18. Which of the following monomers on polymerization give polyoxymethylene also known as polyacetal and which does not exist in isotactic, syndiotactic and atactic forms?
(a) Methoxyethene (b) Formaldehyde
(c) Ethoxyethene (d) Propene

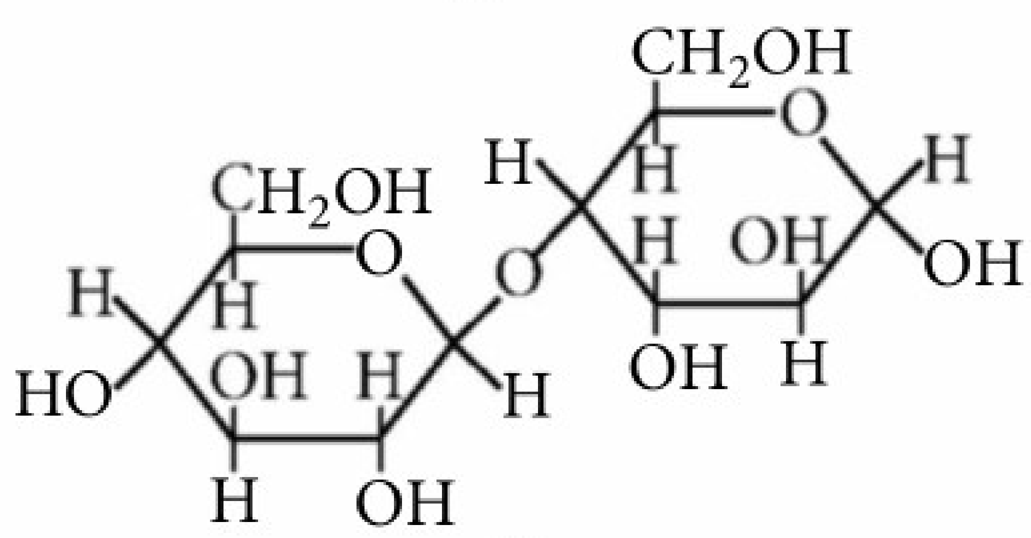
19. The segment of DNA which acts as the instruction manual for the synthesis of protein is
(a) ribose (b) gene
(c) nucleoside (d) nucleotide.

More than One Options Correct Type

20. The correct statement(s) about the following sugar *X* and *Y* is (are)



X



Y

(a) *X* is a reducing sugar and *Y* is a non-reducing sugar
(b) *X* is a non-reducing sugar and *Y* is a reducing sugar
(c) the glycosidic linkage in *X* and *Y* are α - and β - respectively
(d) the glycosidic linkage in *X* and *Y* are β - and α - respectively.

21. Which of the following statements are correct about barbiturates?
(a) Hypnotics or sleep producing agents.
(b) These are tranquilizers.
(c) Non-narcotic analgesics.
(d) Pain reducing without disturbing the nervous system.

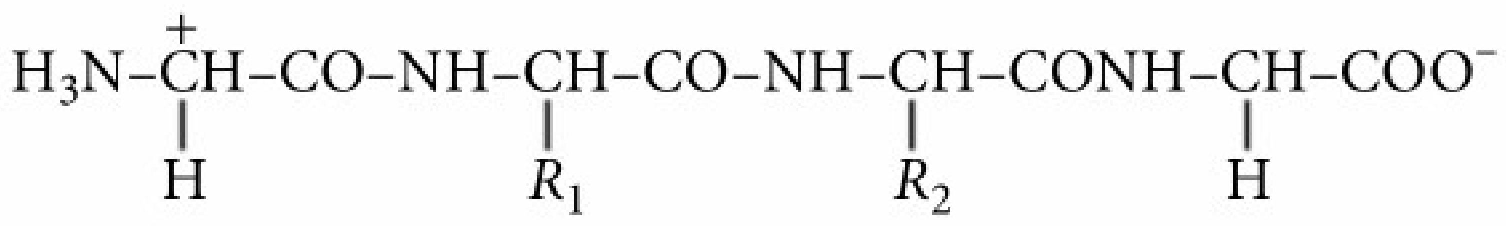
22. Identify the incorrect statement.
(a) The starting material for the manufacture of PVC is obtained by reacting HCl with acetylene.
(b) Natural rubber is a step growth polymer.
(c) Dacron is addition polymer.
(d) Intermolecular forces present in nylon-6, 6 is H-bonding.

23. The correct statements about anomers are
(a) Anomers have different stereochemistry at C-1 (anomeric carbon)
(b) α-D-glucopyranose and β-D-glucopyranose are anomers
(c) Both anomers of D-glucopyranose can be crystallised and purified.
(d) When pure α-D-glucopyranose is dissolved in water its optical rotation slowly changes

Numerical Value Type

24. Total number of lone pairs of electrons in melamine is

25. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH 7.0?



Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

26. The maximum number of neurologically active drugs amongst the following are : Iproniazid, phenelzine, chlordiazepoxide, meprobamate, diclofenac sodium, ibuprofen, naproxen, seconal, paracetamol.

Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage :

Polynucleotides are called nucleic acids. Each nucleotide is made up of three parts, *i.e.*, a pentose sugar, a heterocyclic nitrogenous base and phosphoric acid. Depending upon the nature of sugar whether, ribose or 2-deoxyribose, nucleic acids are called RNA and DNA respectively. In all, there are five nitrogenous bases, two of which are purines while the remaining three are pyrimidines. Out of these five bases, each types of nucleic acid has four of them.

	Column-I		Column-II
A.	Adenine	P.	Purine
B.	Thymine	Q.	Pyrimidine
C.	Uracil	R.	RNA
D.	Ribose	S.	DNA

27. Which of the following has the correct combination considering Column-I and Column-II?
(a) A → P, Q (b) B → Q, S
(c) C → P, R (d) D → Q, P

28. Which of the following has the correct combination considering Column-I and Column-II?
(a) A → P, R, S (b) B → Q, R, S
(c) C → P, Q, S (d) D → P, Q, R

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage :

Drugs designed to cure some ailment in one organ in the body do not affect the other because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity due to release of hydrochloric acid in the stomach. Since antiallergic and antacids drugs work on different receptors therefore, antiallergic dugs remove allergy while antacids remove acidity.

	Column-I		Column-II
A.	Adrenaline	P.	Releases HCl from stomach walls
B.	Noradrenaline	Q.	Causes allergy
C.	Histamine	R.	Hormone
D.	Dopamine	S.	Neurotransmitter

29. Which of the following has the correct combination considering Column-I and Column-II?
(a) A → P, S (b) B → P, Q, S
(c) C → P, Q, R, S (d) D → Q, R

30. Which of the following has the correct combination considering Column-I and Column-II?
(a) A → R, S, P (b) B → R, S
(c) C → P, R (d) D → P, Q, R

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

PROBLEM SET 75

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. A mixture containing 1.12 L of D_2 and 2.24 L of H_2 at NTP is taken inside a bulb connected to another bulb through a stopcock with a small opening. The second bulb is fully evacuated. The stopcock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2. Concentration (% by mass) of the gases in second bulb is

(a) $D_2 = 41.66\%$, $H_2 = 58.33\%$
(b) $D_2 = 58.33\%$, $H_2 = 41.66\%$
(c) $D_2 = 50\%$, $H_2 = 50\%$
(d) $D_2 = 60\%$, $H_2 = 40\%$

2. In the reaction with Tollens' reagent acetylene shows

(a) oxidising property (b) reducing property
(c) basic property (d) acidic property.

3. At 627 °C and one atmosphere pressure SO_3 is partially dissociated into SO_2 and O_2 as $SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$. The density of the equilibrium mixture is 0.925 g/litre. Its degree of dissociation is

(a) 32.20% (b) 30.21% (c) 36.20% (d) 34.08%

4. Surface catalysed reactions that are inhibited by the products obey the rate equation (in some cases), $\frac{dx}{dt} = \frac{K(a-x)}{1+bx}$, where a is the initial concentration of the reactant and K and b are constants. If x is the concentration of products at any time t and the reaction is $A \longrightarrow B$, then $t_{1/2}$ may be calculated by

(a) $\frac{\log 2 + ab(\log 2 - 0.5)}{K}$

(b) $\frac{ab(\log 2 - 0.5)}{\log 2 \times K}$ (c) $\frac{\log 2 \times K}{ab(\log 2 - 0.5)}$

(d) $\frac{K}{\log 2 + ab(\log 2 - 0.5)}$

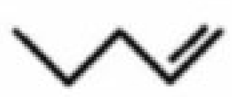
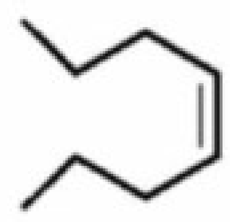
5. When methyl *D*-glucopyranoside is oxidized with periodic acid, how many moles of the oxidizing agent are consumed per mole of the sugar?

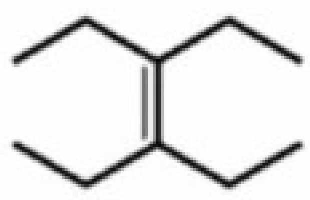
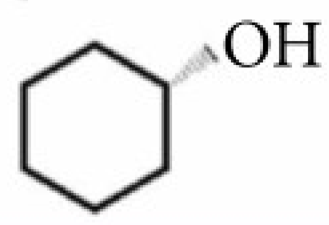
(a) 2 (b) 3 (c) 4 (d) 5

JEE ADVANCED

6. Identify X for the given reaction.

$$X \xrightarrow[\text{2. } Na_2CO_3/CH_3I/DMF]{\text{1. } O_3/Zn\text{-}H_2O} CH_3CH_2CH_2CO_2CH_3$$

(a)  (b) 

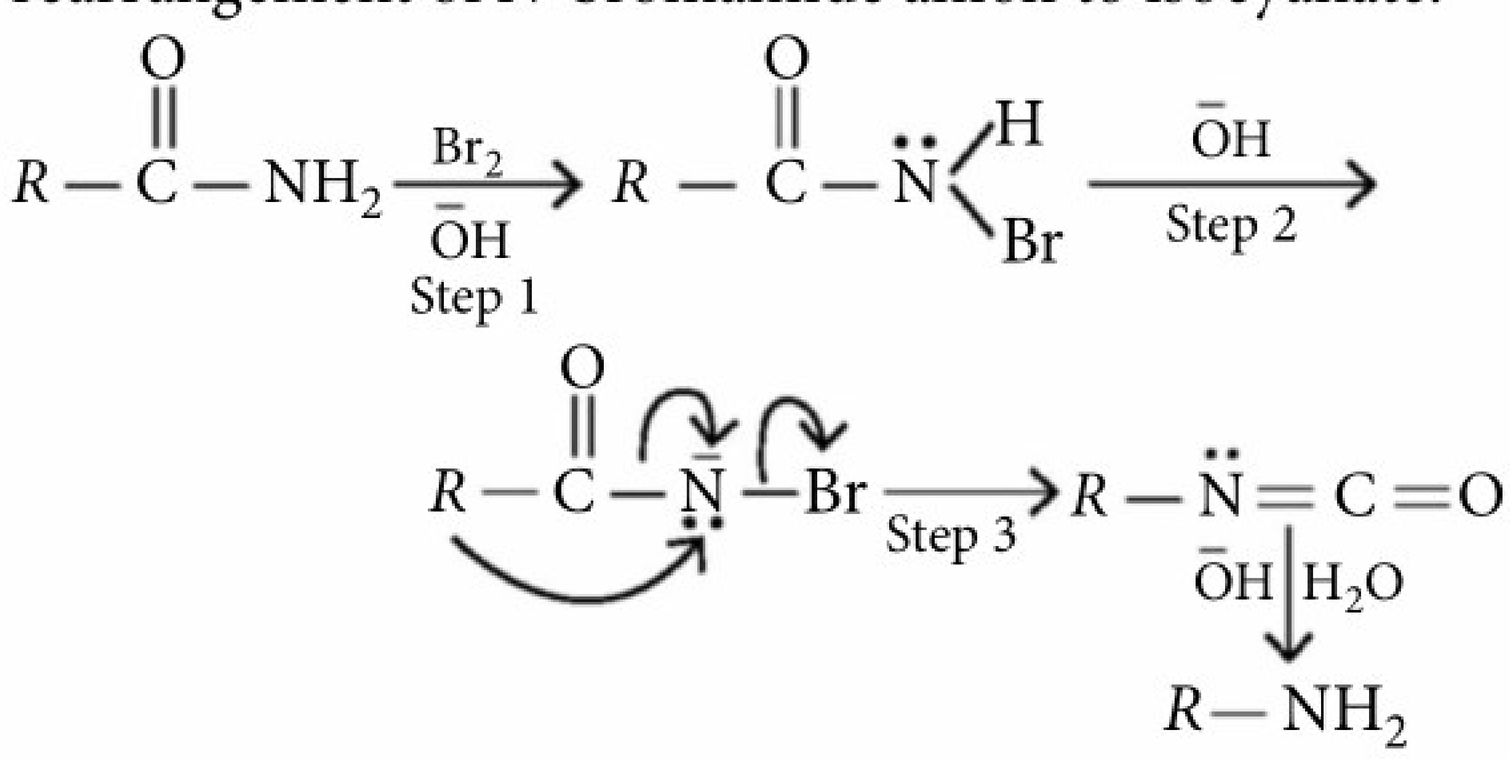
(c)  (d) 

COMPREHENSION

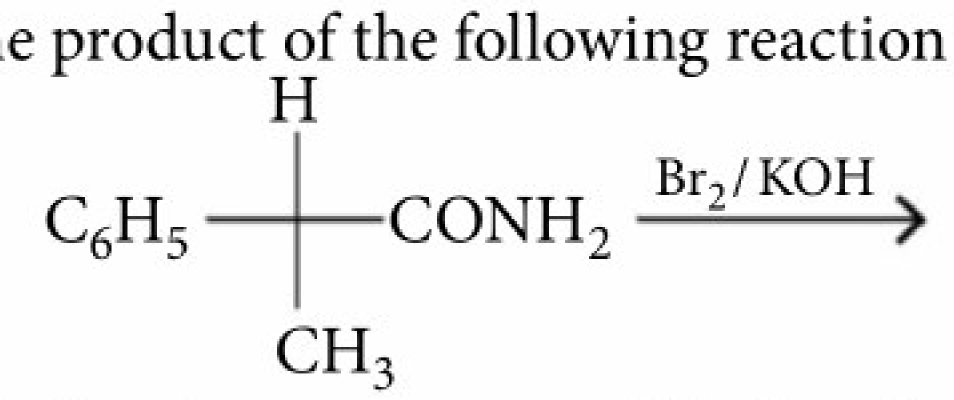
The conversion of an amide into an amine with one carbon atom less by the action of bromine in sodium hydroxide is known as Hofmann bromamide degradation reaction.

$$RCONH_2 \xrightarrow{Br_2/NaOH} R-NH_2$$

The most important feature of the reaction is the rearrangement of *N*-bromamide anion to isocyanate.

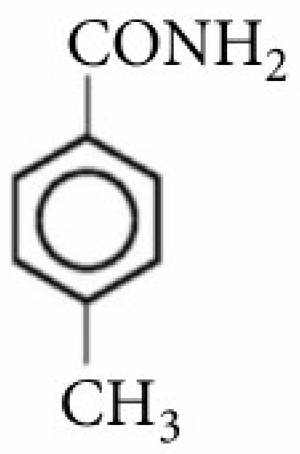


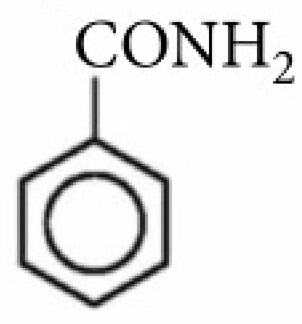
7. The product of the following reaction will be

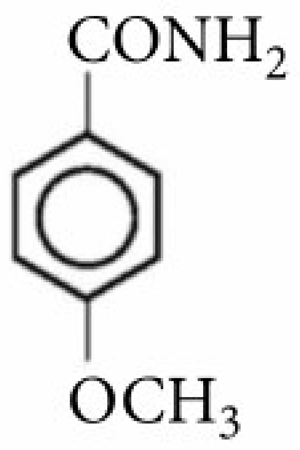


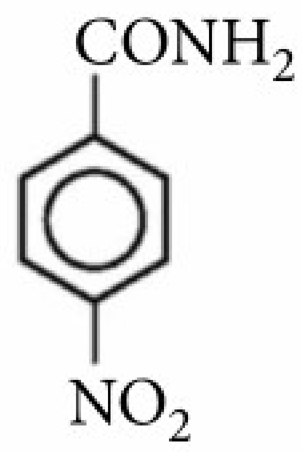
(a) *S*-amine (b) *R*-amine
(c) 50 : 50 mixture of (+) and (–) amine
(d) 30 : 70 mixture of (+) and (–) amine.

8. Which of the following can undergo Hofmann bromamide reaction most easily?

(a) 

(b) 

(c) 

(d) 

NUMERICAL VALUE

9. A certain dye absorbs light of λ = 4530 Å and then emits fluorescence light of 5080 Å. Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, the ratio of no. of quanta emitted out to the no. of quanta absorbed is found to be $x \times 10^{-2}$. What is the value of x?

10. 0.535 g ethanol and acetaldehyde mixture when heated with Fehling's solution gave 1.2 g of a red precipitate. What is the percentage of acetaldehyde in the mixture? (At. wt. of Cu = 63.54).

JOINT ENTRANCE EXAMINATION MAIN – 2020

The National Testing Agency (NTA) will conduct the JEE Main-2020 Examination twice for admission to Undergraduate Programs in NITs, IIITs and other Centrally Funded Technical Institutions (CFTIs), etc. in the next academic year (2020-2021).The First JEE Main-2020 will be conducted in January 2020 between 6th January (Monday) and 11th January (Saturday) 2020 and the Second JEE Main-2020 will be conducted between 3rd April (Friday) and 9th April (Thursday) 2020.

As per the eligibility criteria for B.Arch and B.Planning courses and according to the opinion of Subject Experts, a few changes in the pattern of the question paper(s) and number of question(s) for B.E./B.Tech, B.Arch and B.Planning have been approved by the JEE Apex Board (JAB) for the conduct of JEE Main-2020 Examination.

The pattern of question paper(s) is given below:

PAPER	SUBJECTS	NO. OF QUESTIONS	TYPE OF QUESTIONS	TIMING OF THE EXAMINATION(IST)	
				First Shift	Second Shift
B.E./B.Tech.	Mathematics	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) & 5 Questions with answer as numerical value, with equal weightage to Mathematics, Physics & Chemistry	09:30 a.m. to 12:30 p.m.	02:30 p.m. to 05:30 p.m.
	Physics	25(20+5)			
	Chemistry	25(20+5)			
B. Arch.	Mathematics – Part I	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) & 5 Questions for which answer is a numerical value	09:30 a.m. to 12:30 p.m.	02:30 p.m. to 05:30 p.m.
	Aptitude Test – Part II	50	Objective Type - Multiple Choice Questions (MCQs)		
	Drawing Test – Part III	2	Questions for drawing test		
B. Planning	Mathematics – Part I	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) & 5 Questions for which answer is a numerical value	02:30 p.m. to 05:30 p.m.	
	Aptitude Test – Part II	50	Objective Type - Multiple Choice Questions (MCQs)		
	Planning Based Questions - Part III	25	Objective Type - Multiple Choice Questions (MCQs)		
Note: The timing for those Candidates who opt for B.Arch. and B.Planning (both) will be 02:30 p.m. to 06:00 p.m. (IST)					

The above Examinations will be held in "Computer Based Test" (CBT) Mode only, except that the Drawing Test for B.Arch. will be held in "Pen & Paper" (offline) mode. A candidate may appear in B.E./B.Tech, B.Arch and B.Planning depending upon the course/s he/she wishes to pursue.

The candidates aspiring to take admission to the undergraduate programs at IITs for the year 2020 will also have to appear in B. E. /B. Tech. Paper of JEE Main -2020. Based on the performance in the B.E./B. Tech. of JEE Main-2020, number of top candidates as per the requirement for JEE Advanced-2020 will be eligible to appear in JEE Advanced-2020. Admission to IITs will be based on category -wise All India Rank (AIR) in JEE Advanced,subject to the conditions as would be mentioned in JEE Advanced-2020 website.

For the April JEE Main-2020, a separate notice will be issued later on and the candidates will be required to apply separately. However, candidates are not required to compulsorily appear in both the tests i.e. January JEE Main-2020 and April JEE Main-2020. In case, a candidate appears in both the tests, the better of the two scores will be used for the admissions and eligibility of JEE Advanced-2020.

For more information visit www.jeemain.nic.in

CONCEPT BOOSTER

Hello, My stars over there!! Wish you a very HAPPY DURGA PUJA & DUSSEHRA at first. Festive season is coming. Be safe and be helpful. Don't forget just after the festive month, the EXAM SEASON will be knocking at the door. So keep your eyes at your aim. You still have some time to learn in depth concept. So do that. As always I am there to help you. This article will help you grasp idea about a fantastic concept in thermodynamics. More to come in near future. Take care! All the best.

*Arunava Sarkar

Common Points to Take Care in Thermodynamics

We all know what is Gibbs-Helmholtz relation. It is $\Delta G = \Delta H + T\left[\frac{d}{dT}(\Delta G)\right]_P$.

We are very much accustomed to predict the spontaneity of a reaction based on the value of ΔG. Also we can calculate the value of ΔH if we know ΔG and its variation with temperature. Now, have you ever thought that if you calculate ΔH calorimetrically or otherwise then can you ascertain ΔG? Answer is 'No'. The big reason for this is $\frac{d}{dT}(\Delta G)$ can't be properly ascertained. The reason is as below.

$$\Delta G = \Delta H + T\left[\frac{d}{dT}(\Delta G)\right]_P$$

$$\Rightarrow \left[\frac{d}{dT}(\Delta G)\right]_P = \left[\frac{d}{dT}(\Delta H)\right]_P + T\left[\frac{d^2(\Delta G)}{dT^2}\right]_P + \left[\frac{d}{dT}(\Delta G)\right]_P$$

$$\Rightarrow \left[\frac{d^2(\Delta G)}{dT^2}\right]_P = -\frac{1}{T}\left[\frac{d}{dT}(\Delta H)\right]_P \quad \text{...(1)}$$

$$\Rightarrow \left[\frac{d^2(\Delta G)}{dT^2}\right]_P = -\frac{1}{T}P\cdot\sum V_i\ \bar{C}_{P_i} \quad \text{...(2)}$$

Here, V_i is the stoichiometric co-efficient for i^{th} constituent. It is found to be negative for the reactant and positive for the product. Now, integrating equation (2) from absolute zero to temperature T.

$\therefore$ From equation (2),

$$\int_0^T \frac{d^2(\Delta G)}{dT^2}\,dT = -\int_0^T \frac{1}{T}\sum V_i\,\bar{C}_{P_i}\,dT$$

$$\Rightarrow \left[\frac{d}{dT}(\Delta G)\right]_T = -\int_0^T \frac{1}{T}\sum V_i\,\bar{C}_{P_i}\,dT + \left[\frac{d}{dT}(\Delta G)\right]_{T=0} \quad \text{...(3)}$$

In eqn. (3), the first term in the right hand side can easily be calculated as the variation of $\bar{C}_P$ is known with temperature. But, the value of second term cannot be calculated.

So, $\left[\frac{d}{dT}(\Delta G)\right]_T$ can't be known.

Hence, from a knowledge of ΔH at any given temperature, ΔG can't be known.

Monthly Test Drive CLASS XII ANSWER KEY

1.	(b)	**2.**	(c)	**3.**	(c)	**4.**	(b)
5.	(d)	**6.**	(b)	**7.**	(c)	**8.**	(c)
9.	(b)	**10.**	(c)	**11.**	(d)	**12.**	(b)
13.	(a)	**14.**	(a)	**15.**	(b)	**16.**	(a)
17.	(a)	**18.**	(b)	**19.**	(b)	**20.**	(b,c)
21.	(a,b)	**22.**	(a,b,c)	**23.**	(a,b,c,d)	**24.**	(6)
25.	(4)	**26.**	(9)	**27.**	(b)	**28.**	(a)
29.	(c)	**30.**	(b)				

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

The solution to this problem was given by Nernst as it is known as Nernst Heat Theorem and this is also the precursor of third law of thermodynamics enunciated by Planck's in 1912.

NERNST HEAT THEOREM

According to Gibbs-Helmholtz equation, for a reaction at $T = 0$, $\Delta G = \Delta H$. This is because at $T = 0$, $T\left[\frac{d}{dT}(\Delta G)\right]_P = 0$, where $\frac{d}{dT}(\Delta G)$ may or may not be equal to zero.

Actually, with the lowering in temperature ΔG and ΔH approach each other rapidly. *i.e.*, when $T \to 0$, $\Delta G = \Delta H$.

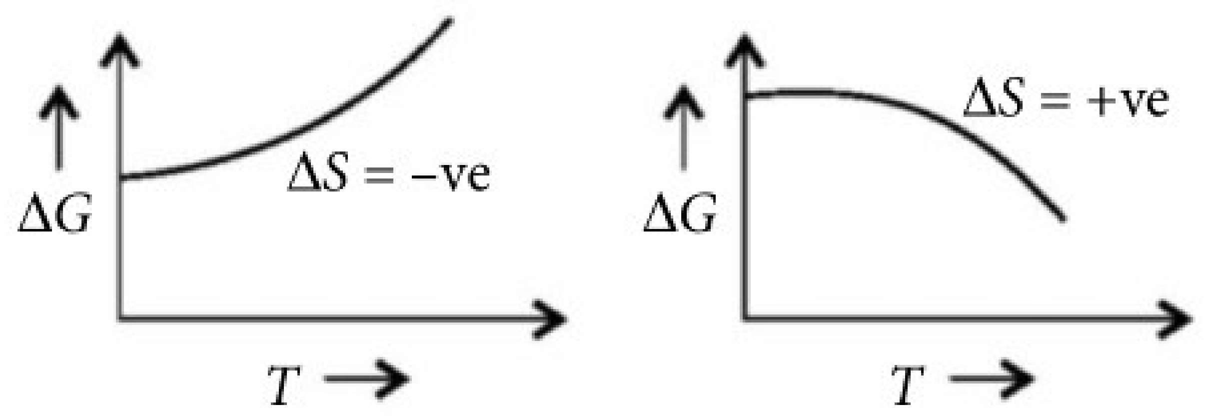
In 1906, Nernst told that for a process in a condensed system $\left[\frac{d}{dT}(\Delta G)\right]$ will be zero at the vicinity of absolute zero.

So, $\lim_{T\to 0}\left[\frac{d}{dT}(\Delta G)\right]_P = 0$

This was indeed a bold postulate.

We know, $\frac{d}{dT}(\Delta G) = -\Delta S$

Entropy is a function of temperature. As ΔS of a reaction can be positive or negative, therefore, ΔG of a reaction may decrease or increase with lowering of temperature *i.e.*,



ΔH can also vary with temperature as $\frac{d}{dT}(\Delta H) = \Delta C_P$ and C_P is a function of temperature.

According to Nernst heat theorem, at absolute zero $\Delta G = \Delta H$ and near the zone of absolute zero, ΔH approaches asymptotically to ΔG. So, $\lim_{T\to 0}\frac{d}{dT}(\Delta H) = 0$

So, overall,

$$\lim_{T\to 0}\frac{d}{dT}(\Delta G) = 0, \lim_{T\to 0}\frac{d}{dT}(\Delta H) = 0$$

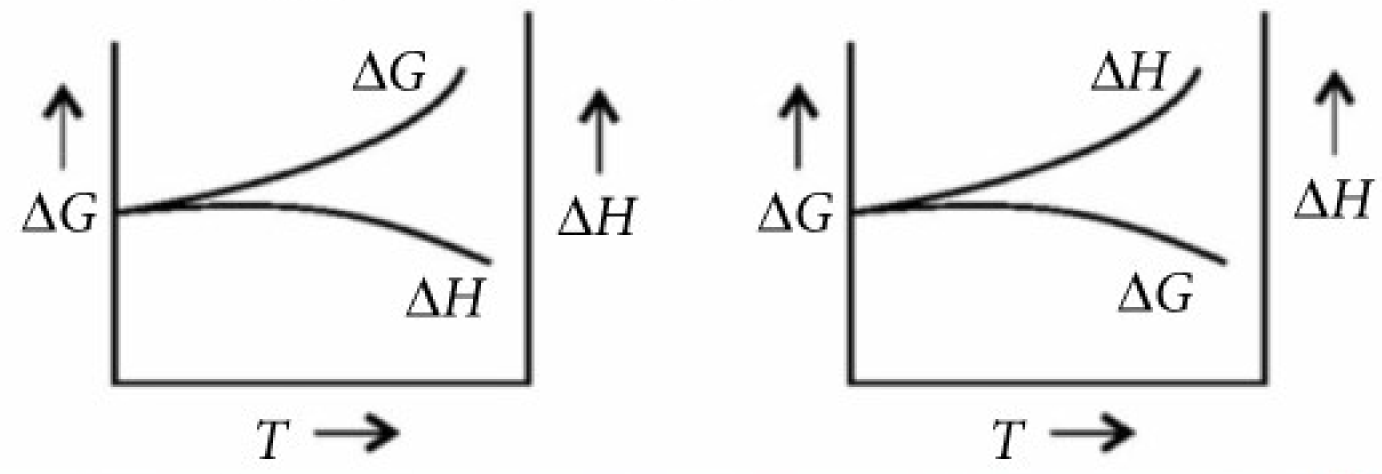
$$\text{Now, } \Delta G - \Delta H = T\frac{d}{dT}(\Delta G)$$

$$\Rightarrow \frac{d}{dT}(\Delta G) - \frac{d}{dT}(\Delta H) = \frac{d}{dT}(\Delta G) + T\frac{d^2}{dT^2}(\Delta G)$$

$$\Rightarrow -\frac{d}{dT}(\Delta H) = T\cdot\frac{d^2(\Delta G)}{dT^2}$$

Now, ΔG converges to limiting value at $T = 0$. So, $T\frac{d^2}{dT^2}(\Delta G)$ and $\frac{d}{dT}(\Delta G)$ will have the same sign.

Therefore, $\frac{d}{dT}(\Delta H)$ and $\frac{d}{dT}(\Delta G)$ have opposite sign.



For the SCIENTIST in YOU

Water harvester makes it easy to quench your thirst in the desert

To deal with water scarcity a major problem worldwide, researchers are close to producing a microwave-sized water harvester that will allow you to pull all the water you need directly from the air even in the hot, dry desert.

Scientists describe the latest version of their water harvester, which can pull more than five cups of water (1.3 litres) from low-humidity air per day for each kilogram (2.2 pounds) of water-absorbing material, a very porous substance called a metal-organic framework, or MOF. That is more than the minimum required to stay alive.

A new MOF design could rapidly adsorb water from even dry air, allowing it to be condensed and collected for drinking. A second-generation MOF can now cycle through adsorption and desorption in 20 minutes, allowing continuous collection of more than a litre per day per kilogram of MOF using solar power.

The harvester cycles 24/7, powered by solar panels and a battery. "It is well known that in order to condense water from air at a low humidity (less than 40 percent relative humidity) you need to cool down the air to below freezing, to zero degrees Celsius, which is impractical. With our harvester, we are doing this at very low humidity without such cooling; there is no other material that can do that," said scientist. "This is not like a dehumidifier, which operates at high relative humidity. Some people say that 0.7 litres is not a lot of water. But it is a lot of water, if you don't have water."

An even larger version of the harvester, one the size of a small refrigerator, will provide 200 to 250 litres of water per day, enough for a household to drink, cook and shower. And in a couple of years, the company hopes to have a village-scale harvester that will produce 20,000 litres per day. All would run on power from solar panels and a battery or off the electrical grid.

Readers' CAFE

Dear Readers,
We have been receiving a lot of queries from students and their parents, so we decided to ease you out by introducing a new column to guide you through your worries, concerns and questions related to your studies and beyond. Readers can send their queries (concerns beyond specific subjects, career guidance, tips for better performance, etc.) by post or by email at editor@mtg.in. The solutions to your queries given by MTG experts will definitely ease your anxiety and provide you a clear vision and a right direction to achieve your goals. Best and most relevant questions will be chosen and published with the sender's name.

V *I am a student of class 12th, aspiring to pursue higher studies in the field of astronomy. However, I am really confused about the correct pathway. What shall I need to do? I am also interested in robotics and manufacturing engineering. I seek career guidance.*

(Tithi Bose, Kolkata, West bengal)

It is good that you are thinking to opt for unique career options. We would like to tell you that 'astronomy' is an observational science rather than a experimental one. Astronomers implement the principles of mathematics and physics to carry out research about the universe.

Astronomy and Astrophysics both the terms are used to refer the same subject. Astronomy is the science of measuring the positions & characteristics of heavenly bodies and astrophysics is the application of physics to understand astronomy. You may join the undergraduate course followed by postgraduate course.

Note : Ph.D. is compulsory to become an astronomer.

You may opt from below mentioned courses after 10 + 2 (Science stream) :

- **Bachelor's courses**
  - B.Sc. in Astrophysics
  - B.Sc. in Astronomy
  - B.Tech. in Electronics and Communication or Electrical Engineering
- **Master's courses**
  - M.Sc. in Astronomy
  - M.Tech. in Astronomy and Space Engineering
- **Doctoral courses**
  - Ph.D. in Astronomy/Astrophysics/Atmospheric Sciences

Now about Robotics :

Two common professions that you can choose in robotics are :

(i) Robotics technicians (ii) Robotics engineers

- **Robotics Technicians**
  - 2 years associate degree in Robotics Technology
- **Robotics Engineer**
  - B.Tech. in Robotics Engineering
  - B.Tech. in Automation Engineering
  - B.Tech. in Mechatronics
  - Bachelor of Engineering in Advanced Robotics

V *My percentage in 12th is 69% having maths, and biology subjects. What will be the best courses for me to pursue?* *(Avantika Rai, Delhi)*

There are many options for a science student. When you have more options, it is always difficult to choose. So, don't get confused, choose wisely. Before choosing your stream, you should know your strengths, aptitude and most importantly, your interest.

Here is a list of courses you can opt for:

- **For Medical**
  - MBBS
  - BDS-Dentistry
  - BAMS-Ayurveda
  - Biotechnology
  - Radiography, etc.
- **For Engineering**
  - Architecture
  - Merchant Navy
  - Nanotechnology
  - Defense Engineering etc.

Other than medical and engineering, you can also opt for Travel and Tourism Management, Banking, Insurance Management Studies, etc.

V *I am a student of class 10th. I am really confused about the stream, which I will have to choose in Class 11. How should I select the right option?* *(Kumkum, Rajasthan)*

The stream that you will choose in Class 11th, will decide your future in the long run.

So, you must take decision wisely keeping in mind your interests, strengths and career options that you want to choose.

- Search the streams available
- Discuss with your parents and teachers.

You just need to go according to your strengths and put some extra efforts to make a successful career.

All the Best

GEAR UP FOR JEE MAIN 2020

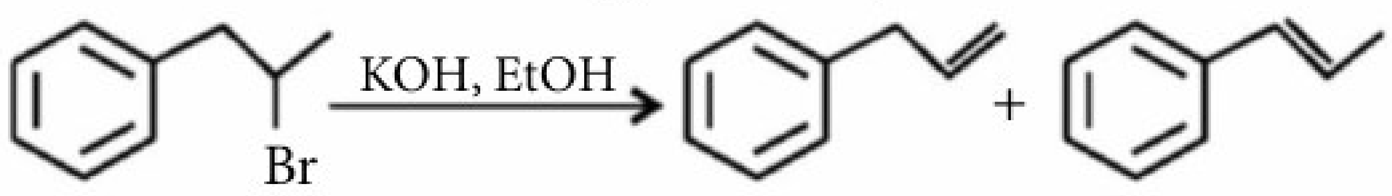
Between 6th to 11th January, 2020

with Numerical Value Type Questions

1. The order of increasing acidic strength for boron hydride is
(a) $B_5H_9 < B_6H_{10} < B_{10}H_{14}$
(b) $B_{10}H_{14} < B_5H_9 < B_6H_{10}$
(c) $B_6H_{10} < B_{10}H_{14} < B_5H_9$
(d) $B_{10}H_{14} < B_6H_{10} < B_5H_9$

2. Which of the following plots does not represent the behaviour of an ideal binary liquid solution of A and B?
(a) Plot of p_B vs X_B is linear.
(b) Plot of p_A *vs* X_A is linear.
(c) Plot of P_{Total} *vs* X_A or X_B is linear.
(d) None of these

3. Consider the following reaction,



(A) (B) (C)

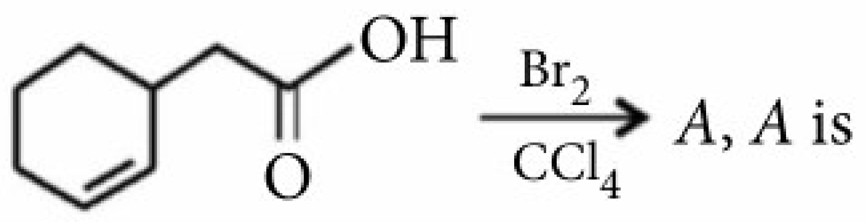
In an experiment, 1.99 g of bromide A on reaction with ethanolic potassium hydroxide gave 1.062 g of a mixture of the olefin B and C. If the ratio of olefins $B : C$ formed is 2 : 1, the yield for their formation respectively are
(a) 60 and 30% (b) 50 and 25%
(c) 66 and 33% (d) 54 and 27%

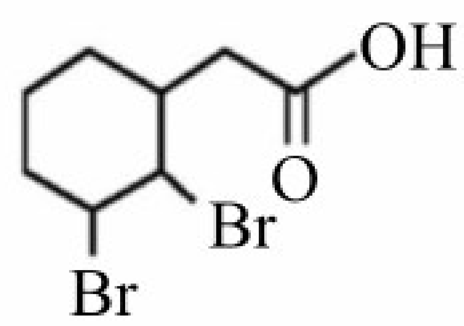
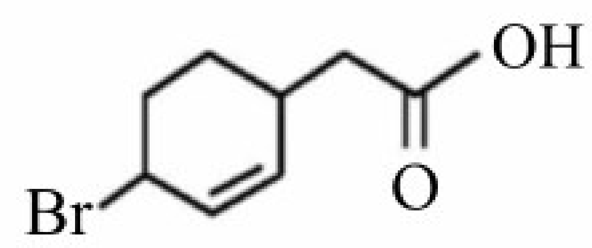
4. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is
(a) $A > B > M$ (b) $B > A > M$
(c) $M > B > A$ (d) $M > A > B$

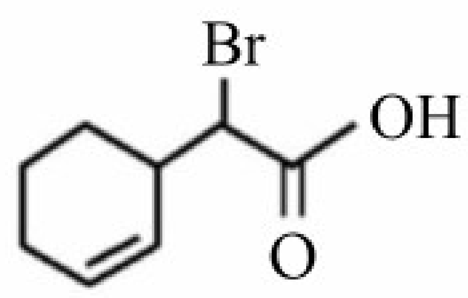
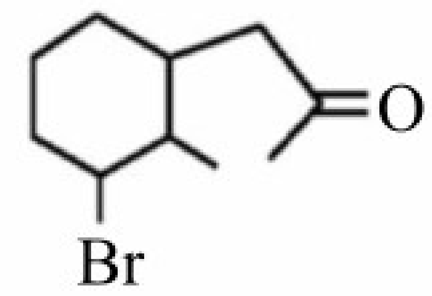
5. For which of the following parameters, the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour)
(a) Heat of vaporisation
(b) Vapour pressure at the same temperature
(c) Boiling points
(d) Gaseous densities at the same temperature and pressure

6. Number of molecules in 100 mL of each of O_2, NH_3 and CO_2 at STP are
(a) in the order $CO_2 < O_2 < NH_3$
(b) in the order $NH_3 < O_2 < CO_2$
(c) the same
(d) in the order $NH_3 = CO_2 < O_2$

7. A coordination complex compound of cobalt has molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of silver nitrate solutions , two moles of AgCl get precipitated. The ionic formula of this complex would be
(a) $[Co(NH_3)_4(NO_2)Cl][(NH_3)Cl]$
(b) $[Co(NH_3)_5Cl][Cl(NO_2)]$
(c) $[Co(NH_3)_5(NO_2)]Cl_2$
(d) $[Co(NH_3)_5][(NO_2)_2Cl_2]$

8. 

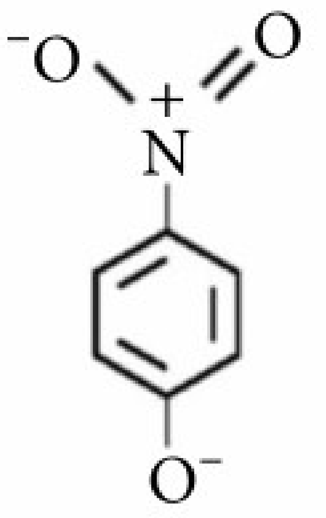
(a)  (b) 

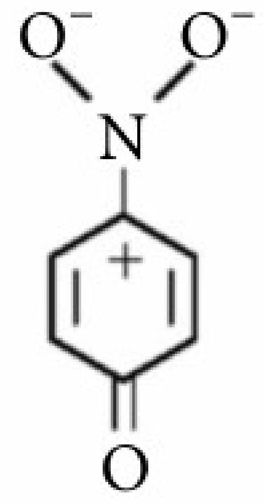
(c)  (d) 

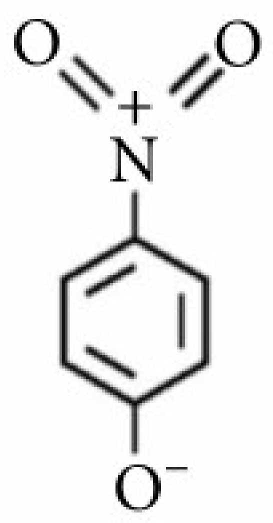
9. Acyclic stereoisomers having the molecular formula, C_4H_7Cl, the geometrical and optical isomers respectively are
(a) 6, 2 (b) 4, 2 (c) 6, 0 (d) 4, 0

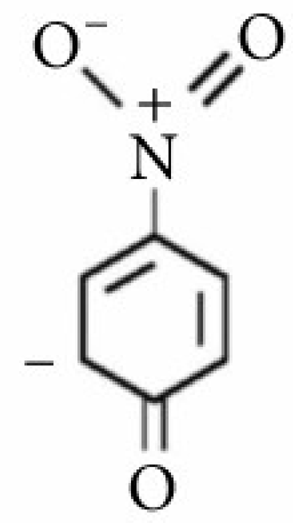
10. Silver is obtained from $Na[Ag(CN)_2]$ by reaction with
(a) Fe (b) Na (c) Zn (d) Au

11. The most unlikely representation of resonance structures of p-nitrophenoxide ion is

(a) 

(b) 

(c) 

(d) 

12. If the de Broglie wavelength of a particle of mass m is 100 times its velocity, then its value in terms of its mass (m) and Planck's constant (h) is

(a) $\frac{1}{10}\sqrt{\frac{m}{h}}$ (b) $10\sqrt{\frac{h}{m}}$ (c) $\frac{1}{10}\sqrt{\frac{h}{m}}$ (d) $10\sqrt{\frac{m}{h}}$

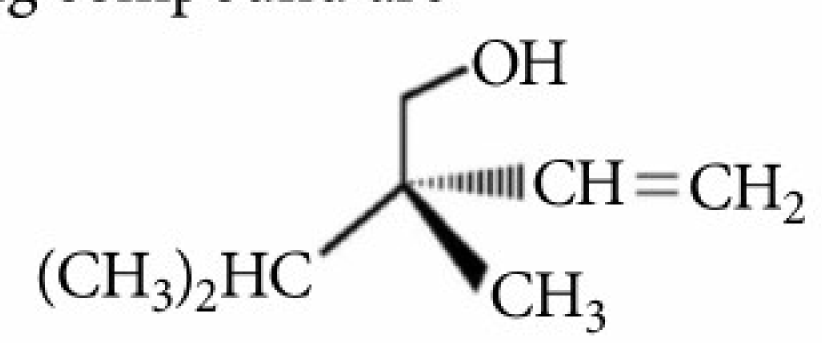
13. A soluble compound of a poisonous element M, when heated with Zn/H_2SO_4 gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silver mirror of element M, then M and N will be

(a) As and AsH_3 (b) P and PH_3
(c) N and NH_3 (d) Sb and SbH_3

14. The pair of which salts is expected to have same colour in their freshly prepared aqueous solutions.

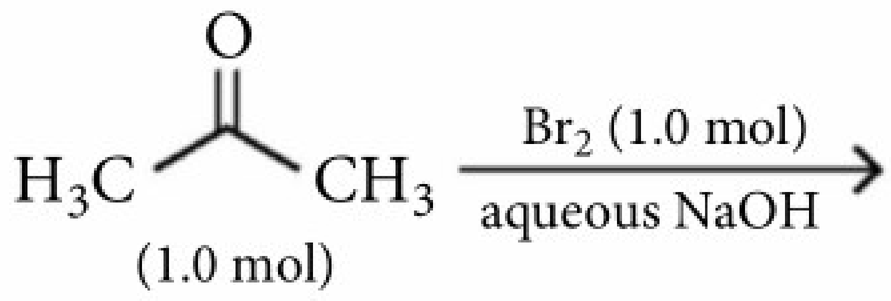
(a) $VOCl_2$, $CuCl_2$ (b) $CuCl_2$, $FeCl_2$
(c) $FeCl_2$, $VOCl_2$ (d) $MnCl_2$, $FeCl_2$

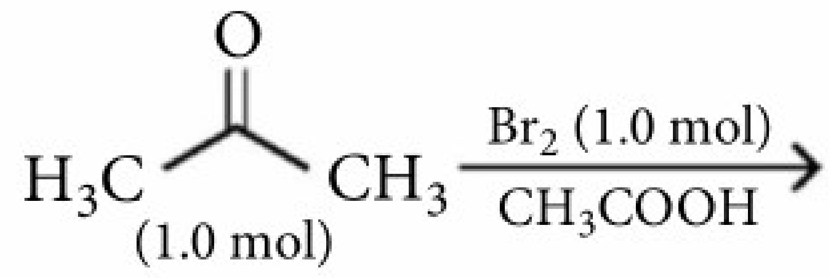
15. The Cahn-Ingold-Prelog (CIP) priorities of the group and the absolute configuration (R/S) of the following compound are

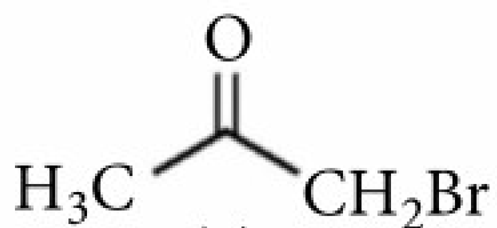


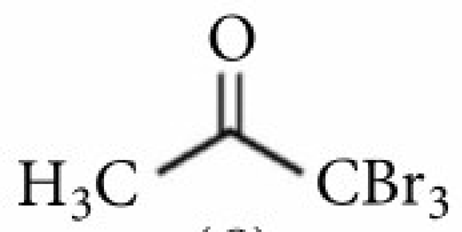
(a) $-CH_2OH > -CH(CH_3)_2 > -CH = CH_2 > -CH_3$ and S
(b) $-CH_2OH > -CH = CH_2 > -CH(CH_3)_2 > -CH_3$ and S
(c) $-CH_2OH > -CH = CH_2 > -CH(CH_3)_2 > -CH_3$ and R
(d) $-CH_2OH > -CH(CH_3)_2 > -CH = CH_2 > -CH_3$ and R.

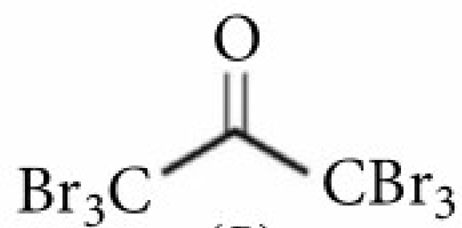
16. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

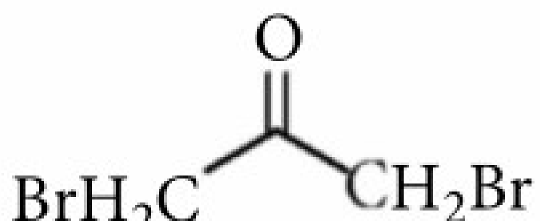
Reaction I : 

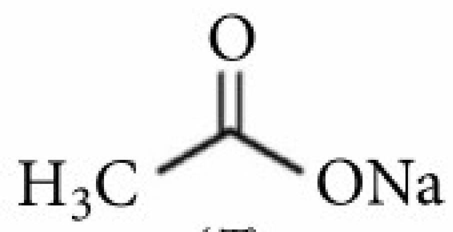
Reaction II: 


(P)


(Q)


(R)


(S)


(T)

$CHBr_3$
(U)

(a) Reaction I : P and Reaction II : P
(b) Reaction I : U, acetone and Reaction II : Q, acetone
(c) Reaction I : T, U, acetone and Reaction II : P
(d) Reaction I : R, acetone and Reaction II : S, acetone

17. Consider the following equation for a cell reaction

$A + B \rightleftharpoons C + D$ $\quad E° = x$ V, $K_{eq} = K_1$
$2A + 2B \rightleftharpoons 2C + 2D$ $\quad E° = y$ V, $K_{eq} = K_2$

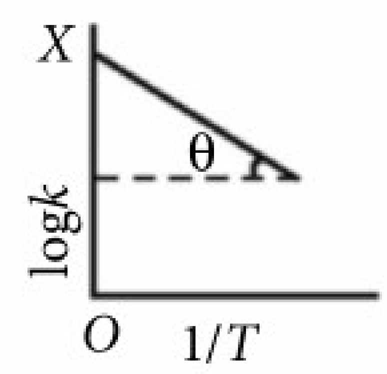
then

(a) $x = y$; $K_1 = \frac{1}{K_2}$ (b) $x = y$; $K_1 = K_2^2$
(c) $x = y$; $K_2 = K_1^2$ (d) $x = 2y$; $K_1 = 2K_2$

18. Out of N_2O, SO_2, I_3^+, I_3^-, H_2O, NO_2^- and N_3^-, the linear species are

(a) NO_2^-, I_3^+, H_2O (b) SO_2, I_3^+, N_3^-
(c) N_2O, I_3^-, N_3^- (d) N_3^-, I_3^+, SO_2

19. Graph between log k and $\frac{1}{T}$ is a straight line with $OX = 5$, $\tan\theta = \left(\frac{1}{2.303}\right)$. Hence, E_a will be



(a) 2.303×2 cal
(b) $\frac{5}{2.303}$ cal
(c) -2 cal (d) none of these.

20. One mole of oxygen at 273 K and one mole of sulphur dioxide at 546 K are taken in two separate containers, then,

(a) kinetic energy of O_2 > kinetic energy of SO_2
(b) kinetic energy of O_2 < kinetic energy of SO_2
(c) kinetic energy of both are equal
(d) none of the above.

Numerical Value Type

21. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2g/cc then find the radius of metal atom. (N_A = 6 × 10^{23}). Give the answer in pm.

22. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

23. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 348 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

24. All the energy released from the reaction $X \rightarrow Y$, $\Delta_rG° = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E° = -0.25$ V.

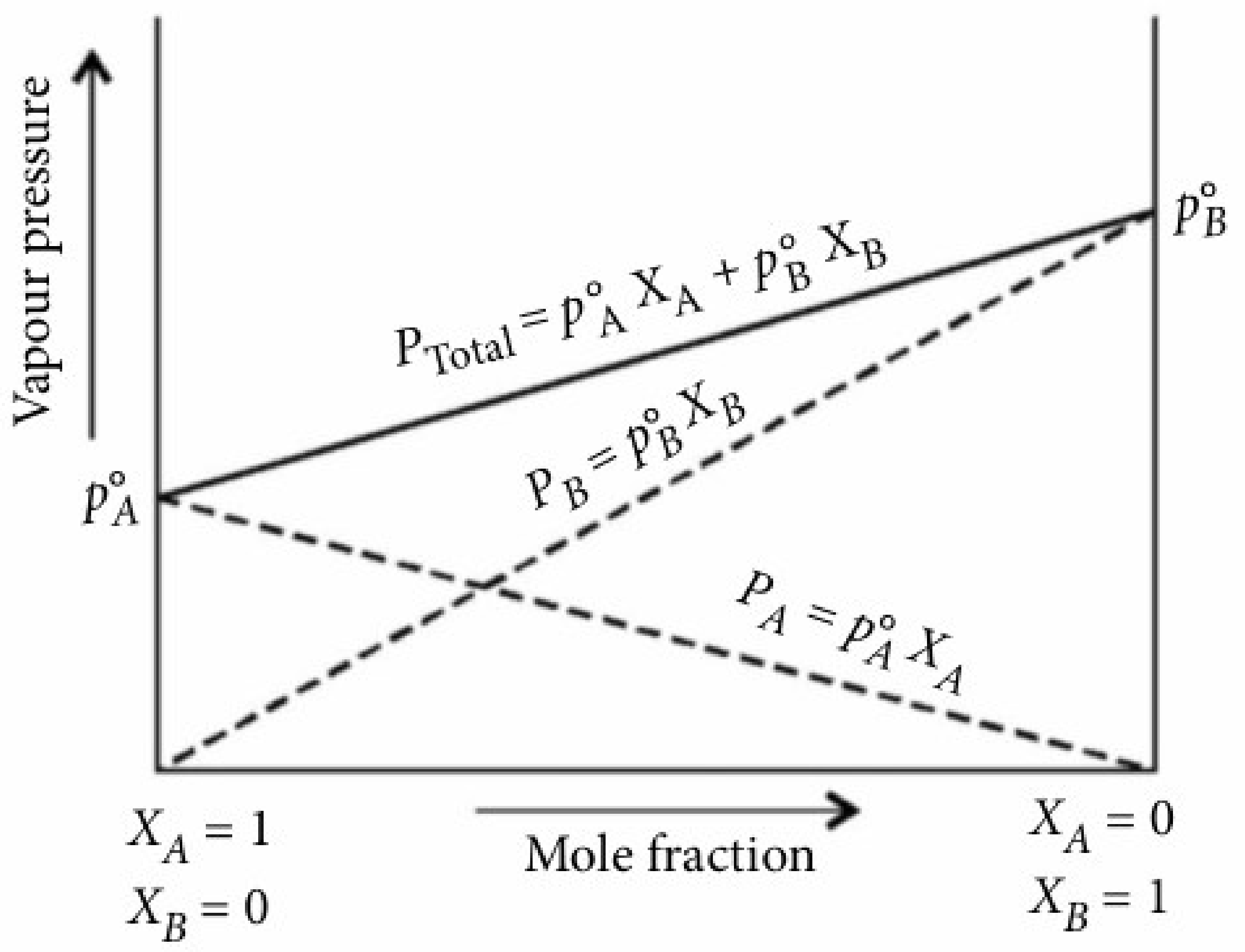
Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is [F= [illegible] C mol^{-1}]

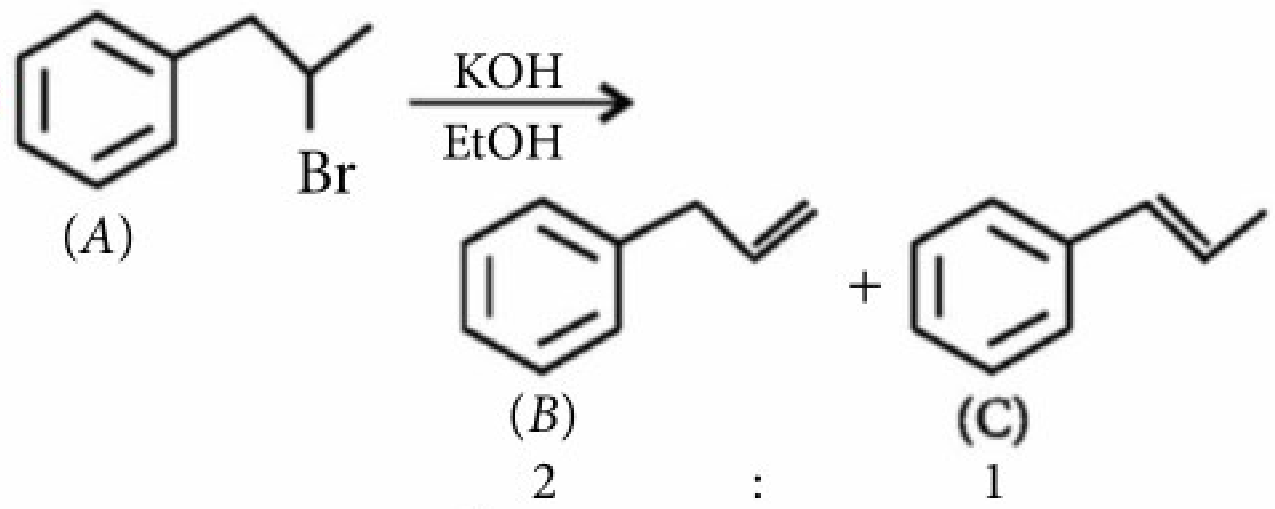
25. A decapeptide (Mol. wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

SOLUTIONS

1. (a) : Acidic strength of boranes ∝ No. of B-atoms in the compound.

2. (c) : Plot of P_{Total} *vs* $X_A + X_B$ is linear.



3. (a) : 

M.wt. of A = 199 g mol^{-1}

M.wt. of B or C = 118 g mol^{-1}

According to balanced chemical equation 199 g of A give product mixture = 118 g

∴ 1.99 g of A will give products = $\frac{118 \times 1.99}{199} = 1.18$ g

But yield = 1.062 g

So, percentage yield = $\frac{1.062}{1.18} \times 100 = 90\%$

Since, ratio of B and C is 2 : 1

∴ Yield of B = 60% and yield C = 30%

4. (c) : C removes oxygen from AO and BO but not from MO. So, C is better reducing agent than A and B but not than M. B removes oxygen from AO, B is better reducing agent than A. Better reducing means more active.

Hence, the correct order is $M > B > A$.

5. (d) : Vapour density $= \frac{\text{Molecular weight}}{2}$

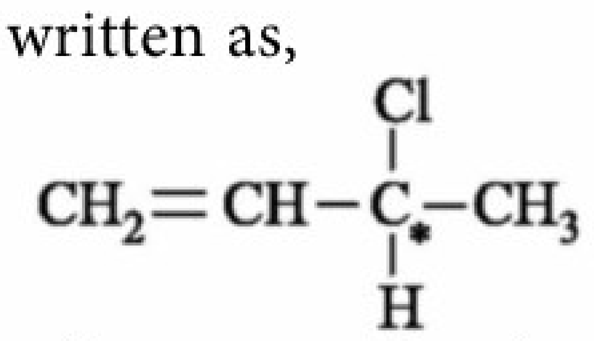
As both the compounds have same molecular weights, both will have the same vapour density. Hence, gaseous density of both ethanol and dimethyl ether would be same under identical conditions of temperature and pressure. The rest of these three properties; vapour pressure, boiling point and heat of vaporization will different in isomers of C_2H_5OH and CH_3COCH_3.

6. (c) : Equal volume of all gases at STP contain equal number of molecules.

7. (c) : Since one mole of compound produces three mole of ions, there must be two ions outside the coordination sphere. Since two Cl-atoms are ionizable, the probable formula of the compound is $[Co(NH_3)_5(NO_2)]Cl_2$.

8. (d)

9. (a) : Acyclic stereoisomers having molecular formula C_4H_7Cl can be written as,



One asymmetric carbon

Therefore, number of optical isomers = $2^n = 2^1 = 2$

Two geometrical isomers of each compound are possible for the following structures :

$ClHC{=}CH{-}CH_2{-}CH_3$, $ClH_2C{-}CH{=}CH{-}CH_3$

and $CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_3$

10. (c) : $2[Ag(CN)_2]^-_{(aq)} + Zn_{(s)} \longrightarrow 2Ag + [Zn(CN)_4]^{2-}_{(aq)}$

11. (c) : In case of nitrogen atom the valence shell cannot have more than 8 electrons because of absence of d-orbitals in it.

12. (b) : Let the velocity of particle be x.

So, de Broglie wavelength (λ) = $100x$

$$x = \frac{\lambda}{100}$$

$$\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{h \times 100}{m \times \lambda} \Rightarrow \lambda^2 = 100\frac{h}{m} \text{ or } \lambda = 10\sqrt{\frac{h}{m}}$$

13. (a) : The poisonous element may be As. Thus, we have

$$\underset{\text{(Soluble)}}{AsCl_3} + 6[H] \xrightarrow{Zn/H_2SO_4} \underset{\substack{\text{'N'} \\ \text{(Poisonous gas)}}}{AsH_3} + 3HCl$$

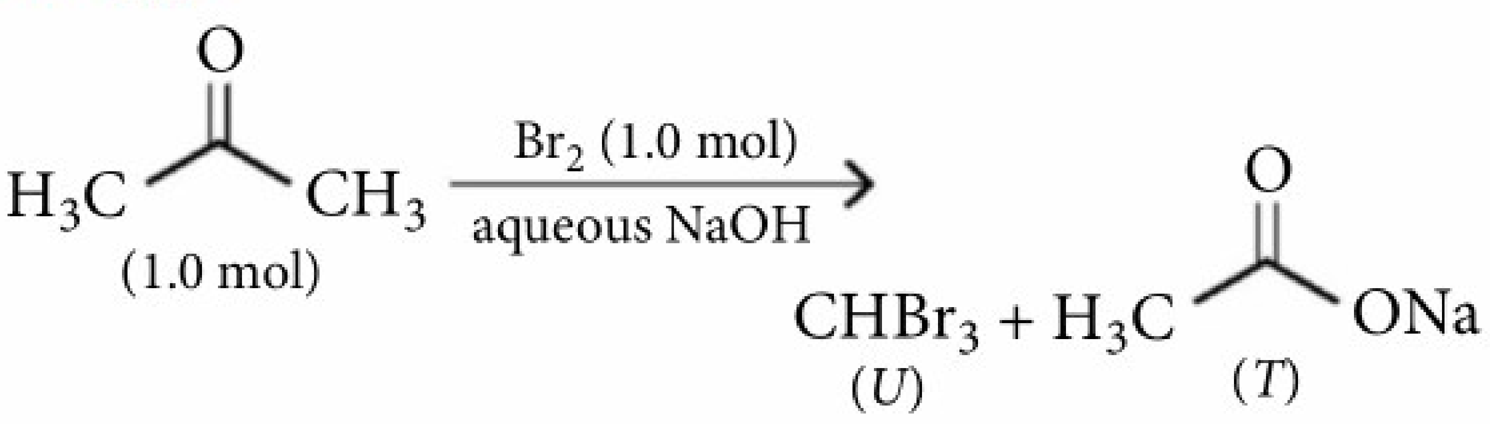
$$2AsH_3 \xrightarrow{\Delta} \underset{\substack{\text{'M'} \\ \text{(Silver mirror)}}}{2As} + 3H_2\uparrow$$

Hence M = As and N = AsH_3.

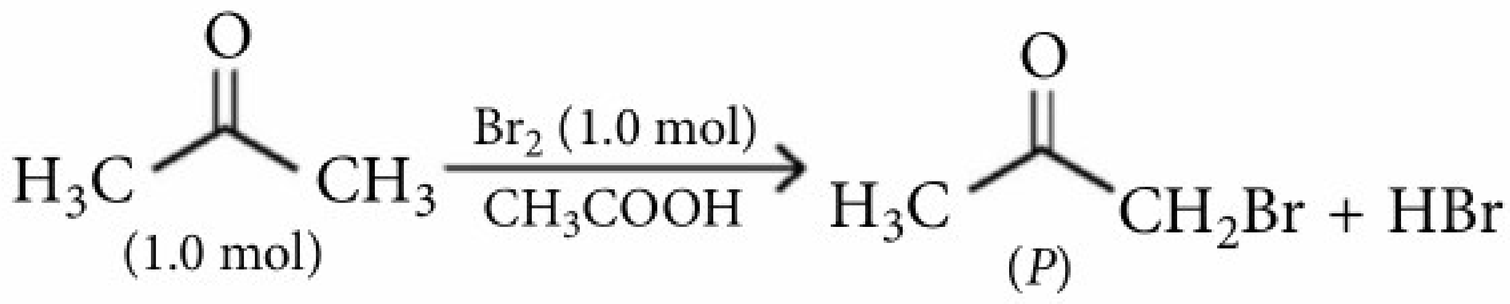
14. (a)

15. (b) : Priority number of atoms bonded to chirality centre is decided on the basis of their atomic number. Higher the atomic number, higher is the priority. Ethynyl or vinyl group has priority over isopropyl group.

16. (c) : Reaction I :



Reaction II :



17. (c) : $K_1 = \frac{[C][D]}{[A][B]}; K_2 = \frac{[C]^2[D]^2}{[A]^2[B]^2}$

therefore $K_2 = K_1^2$

Since on multiplying equation by any stoichiometric coefficient, electrode potential value does not get multiplied, therefore $x = y$.

18. (c) : **N_2O : $\bar{N}{=}\overset{+}{N}{=}O$**

Both N are sp hybridised and are arranged in linear shape.

I_3^- : I_3^- ($I - I \leftarrow I^-$) is a trihalide have one covalent and one coordinate bond which involve half filled $5p$ orbital and vacant $5d$ orbital respectively. It undergoes sp^3d hybridization with 2 bp and 3 lp giving trigonal bipyramidal geometry with linear structure.

N_3^- : Central N atom is sp hybridised with 2 bp (terminal N atoms with sp^2 hybridisation) give a linear shape to azide (N_3^-) ion.

19. (c) : $\log k = \log A - \frac{E_a}{2.303RT}$

$$\text{Slope} = \frac{-E_a}{2.303R} = \frac{1}{2.303}\text{(given)}$$

$E_a = -2.303\ R \times \text{slope} = R = -2$ cal

20. (b) : As, $K.E. = \frac{3}{2}RT$

$\therefore\ K.E. \propto T$

$$\Rightarrow \frac{K.E._{O_2}}{K.E._{SO_2}} = \frac{T_{O_2}}{T_{SO_2}} = \frac{273\text{ K}}{546\text{ K}} = \frac{1}{2} \Rightarrow K.E._{SO_2} = 2K.E._{O_2}$$

$\therefore\ K.E._{SO_2} > K.E._{O_2}$

21. (216.5) : $\rho = \frac{Z \times m}{N_A V}$

$$Z = \frac{\rho N_A a^3}{m} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} \approx 2$$

Value of Z represents that the element must have body-centred cubic structure. For bcc structure, atomic radius

$$= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 5\text{ Å} = 2.165\text{ Å} = 216.5\text{ pm}$$

22. (9) : Given, $C_V = 2.5\text{ kJ K}^{-1} = 2500\text{ J K}^{-1}$

$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$ K

ΔH due to combustion of 3.5 g gas = $C_V \times \Delta T$

= 2500 × 0.45 = 1125 J

Given, molecular weight of gas = 28

$\therefore$ 28 ≡ 1 mole

Hence, ΔH due to combustion of 1 mole of gas

$$= \frac{1125}{3.5} \times 28 = 9000 \text{ J}$$

$\therefore$ ΔH in kJ mol^{-1} = 9000 J mol^{-1} or 9 kJ mol^{-1}

23. (5.14) : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$\begin{array}{lcc} t=0 & 1 & 0 \\ t_{eqm} & 1-x & 2x \end{array}$$

Total = 1 − x + 2x = 1 + x

As, $PV = nRT = \frac{w}{M}RT$

$$P = \frac{w}{V} \times \frac{1}{M}RT\,;\ P = \frac{\rho}{M}RT$$

$$\therefore\ M = \frac{\rho}{P}RT = \frac{1.84}{1} \times 0.0821 \times 348 = 52.57$$

$$x = \frac{M_{\text{cal}} - M_{\text{obs}}}{M_{\text{obs}}} = \frac{92 - 52.57}{52.57} = 0.750$$

$$\text{Hence, } K_P = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2x}{1+x} \cdot p\right)^2}{\left(\frac{1-x}{1+x} \cdot p\right)}$$

$$= \frac{4x^2}{1-x^2}p = \frac{4(0.750)^2}{1-(0.750)^2}(1 \text{ atm}) = 5.14 \text{ atm}$$

24. (4) : Given :

$X \longrightarrow Y$; $\Delta_r G°$ = − 193 kJ mol^{-1}

$M^+ \longrightarrow M^{3+} + 2e^-$; $E°$ = −0.25 V

F = 96500 C mol^{-1}

Let 193 kJ is used for oxidising x moles of M^+.

For 1 mole of M^+, $\Delta G° = -nFE°$

$= -2 \times 96500 \times (-0.25) = 48250$ J mol^{-1} = 48.25 kJ mol^{-1}

Thus, no. of moles of M^+ oxidized when one mole of X is converted to $Y = \frac{193}{48.25} = 4$

25. (6) : Decapeptide + $9H_2O \longrightarrow$

Glycine + Alanine + Phenylalanine

Total wt. of amino acids after addition of 9 moles of H_2O

= 796 + (9 × 18) = 958

Let n units of glycine are present in the decapeptide, then number of glycine unit calculated as,

$$\frac{n \times 75}{958} \times 100 = 47 \Rightarrow n = 6$$

Rank Enhancer

This column is specially designed to make your concepts crystal clear.

Aromaticity

Classification of Compounds Based on Aromaticity

- Aromatic
  - Homocyclic (*A*)
    - Monocyclic
    - Bicyclic
    - Polycyclic
    - Annulene
    - Polygon
  - Heterocyclic (*B*)
- Anti-aromatic
- Non-aromatic
  - Conjugated
  - Non-conjugated

- Comparative study of Aromatic, Anti-aromatic and Non-aromatic compounds :

Aromatic	Anti-aromatic	Non-aromatic
Cyclic	Cyclic	All compounds which are neither aromatic nor anti-aromatic.
Conjugated and delocalised over entire ring	Conjugated and delocalised over entire ring	
Planar	Planar	
$(4n + 2)$ number of delocalising electrons	$4n$ number of delocalising electrons	

- Order of stability : Aromatic > Non-aromatic > Anti-aromatic.

CLEAR YOUR MISCONCEPTS

Aromatic Compounds

1. Delocalising electrons may not be always π electrons. They can be lone pair of electrons.

Example :

Here, *lp* on 'N' is also delocalising.

$\therefore$ Total number of delocalising electrons

$= 2 \times (2\pi \text{ bonds}) + 2\ (1\ lp \text{ on N})$

$= 2 \times (2) + 2(1) = 6e^-$

2. If an atom contains two or more *lp* count only one *lp*, delocalising electrons.

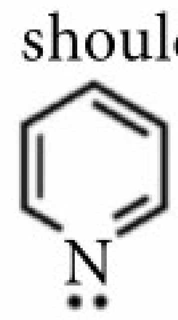
Example :  Here, 'S' contains two *lp*, but only one *lp* participated in delocalisation.

$\therefore$ Total number of delocalising electrons

$= 2 \times (2\pi \text{ bond}) + 2\ (1\ lp)$

$= (2 \times 2) + (2 \times 1) = 6e^-$

3. Sometimes lone pair may not be involved in delocalisation if it is associated with π-bond. Hence should not be counted in delocalising electrons.



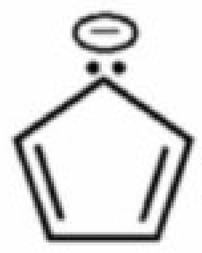
Here *lp* on 'N' do not involve in delocalisation

By K. Vijay Bhasker, Senior faculty at Sri Chaitanya Educational Institution, Visakhapatnam

because of presence of π bond on 'N' which is used in delocalisation.

$\therefore$ Total number of delocalising electrons

$= 2(3\pi \text{ bonds}) + 0 \times (1\ lp) = 6\ lp$

4.  If carbanion is present in conjugation.

It is considered as planar due to involvement of *lp* in conjugation, it looses non-planarity character.

$\therefore$ Total number of delocalising electrons

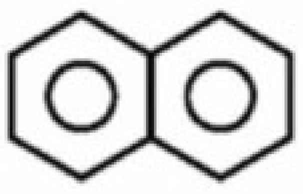
$= 2(2\pi \text{ bonds}) + 2(1\ lp)$

$= (2 \times 2) + (2 \times 1) = 6e^-$

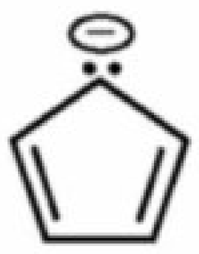
Types of Aromatic Compounds :

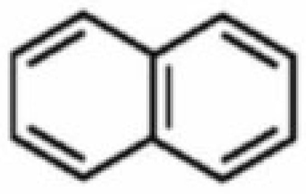
(A) Homocyclic aromatic compounds : Aromatic compounds in which all corners occupied by single type of atoms (*i.e.,* 'C')

Example :

 ,  , 

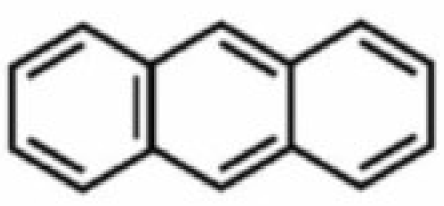
They are further subdivided into five types :

(i) Monocyclic :  , 

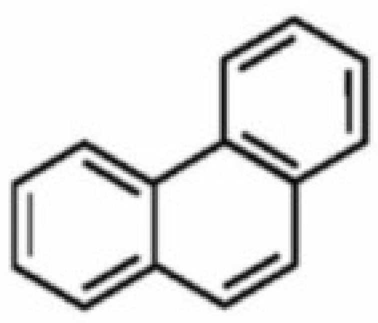
(ii) Bicyclic : 

Naphthalene

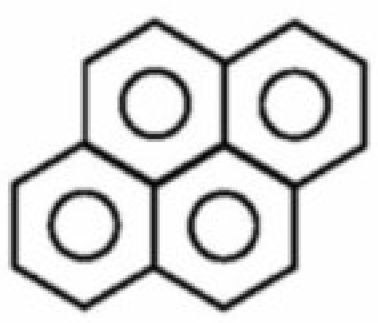
(iii) Polycyclic :



Anthracene



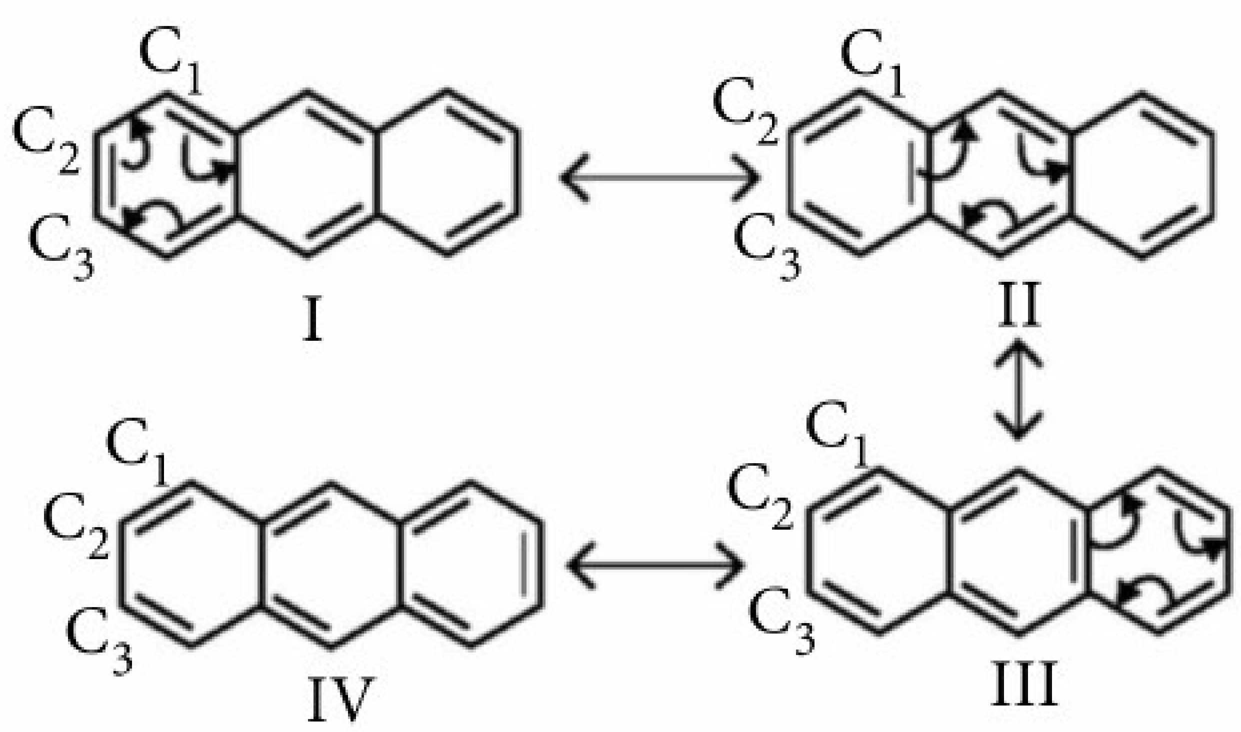
Phenanthrene



Pyrene

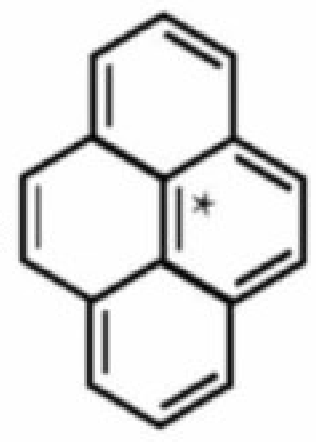
Special Points for JEE Advanced and AIIMS

(a) In anthracene bond order is not same for all bonds between 'C' atoms.



Bond order of $C_1 - C_2$ bond $= \frac{1+2+2+2}{4} = \frac{7}{4} = 1.75$

Bond order of $C_2 - C_3$ bond $= \frac{2+1+1+1}{4} = \frac{5}{4} = 1.25$

(b) In pyrene 

*Marked π bond not used in delocalisation.

Hence, total number of delocalised electrons $= 7 \times (2\pi\ e^-)$

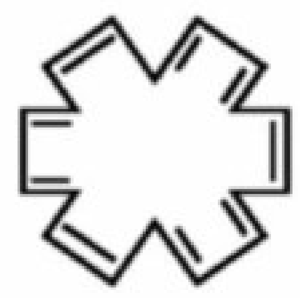
$= 14e^-$

(iv) Annulenes : Completely conjugated monocyclic polyene containing an even number of carbon atoms are called annulene.

Molecular formula $= C_nH_n$

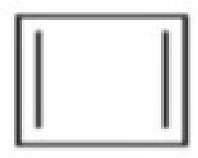
where, n = number of π bonded electrons = number of 'C' atoms

[6] Annulene



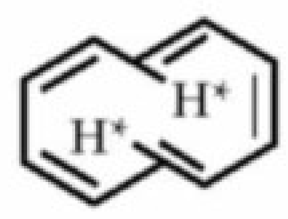
[18] Annulene

Note :



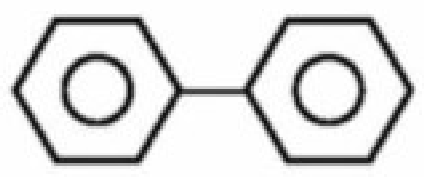
[4] Annulene
Anti-aromatic

Similarly [12] annulene is also anti-aromatic.



[10] Annulene

Non-aromatic due to steric hinderance between *H looses planarity.

(v) Polygon :  

Biphenyl Terphenyl

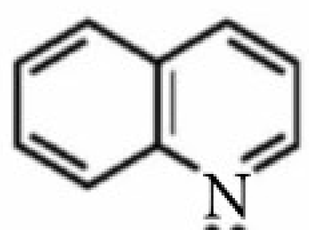
(B) Heterocyclic aromatic compounds : These are ring compound containing one or more hetero atoms in the carbon ring.

Thiophene

Furan

Pyrrole

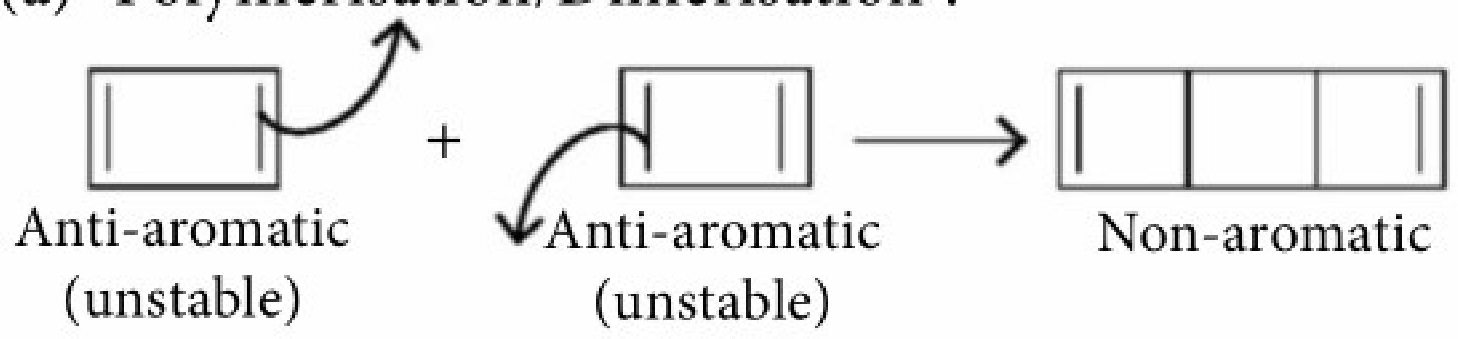
Pyridine



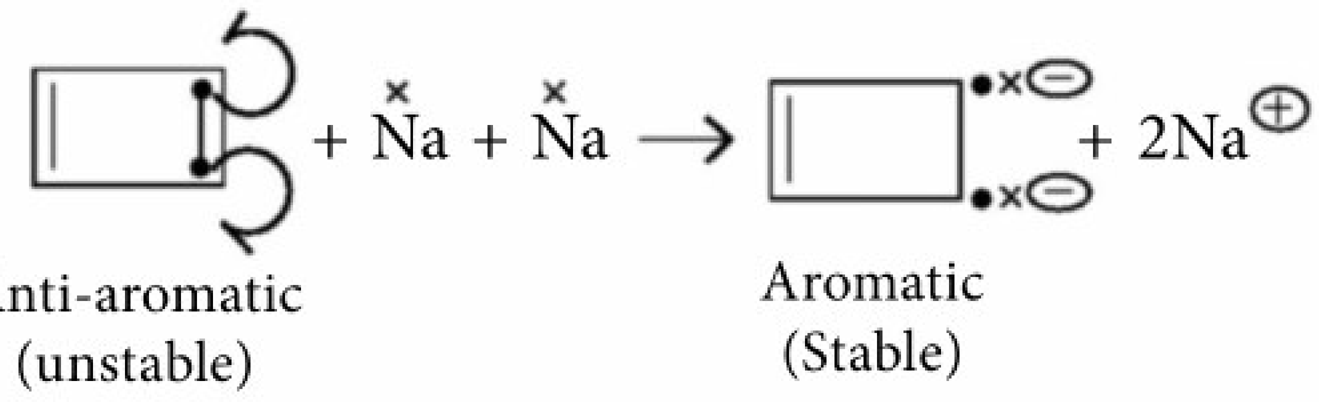
Quinoline

Anti-aromatic compounds : These are most unstable compounds. They get stabilised by any of following 3 methods :

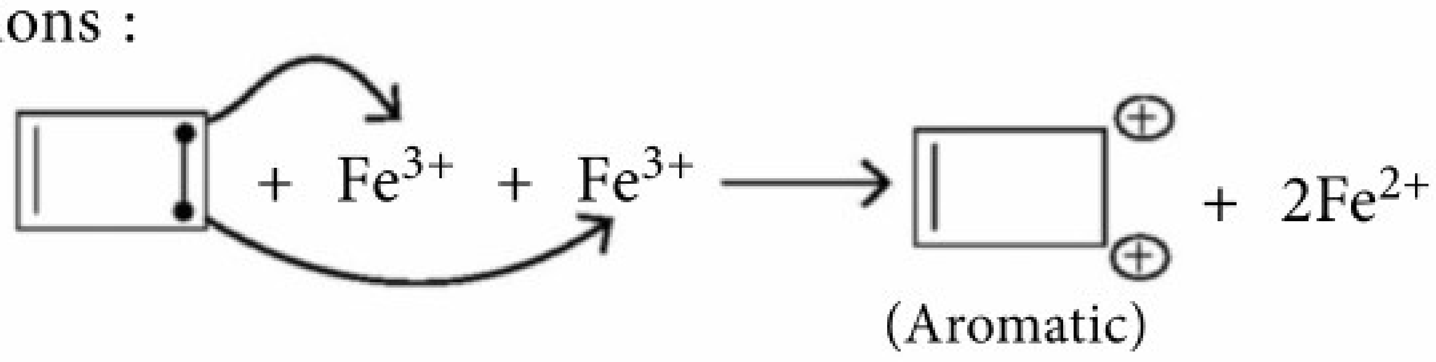
(a) Polymerisation/Dimerisation :



(b) By undergoing reduction on reaction with metals :

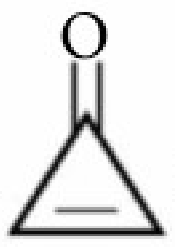


(c) By undergoing oxidation on reaction with metal ions :



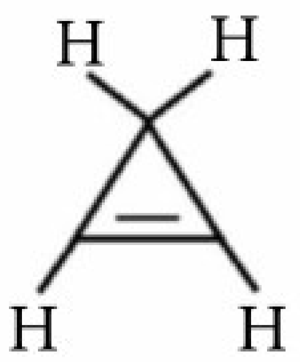
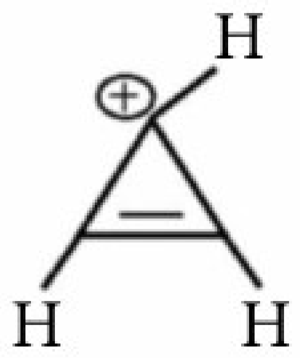
QUESTIONS FOR PRACTICE

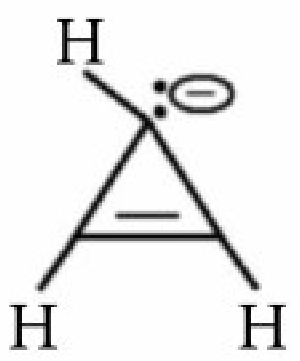
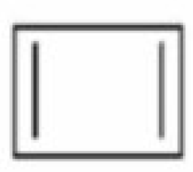
Single Option Correct Type

1. Cyclopropenone,  is

(a) aromatic (b) non-aromatic
(c) anti-aromatic (d) annulene.

2. Which of the following is aromatic ?

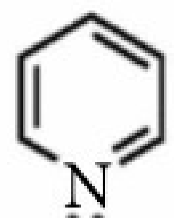
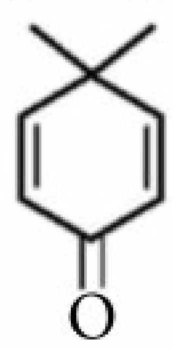
(a)  (b) 

(c)  (d) 

3. Number of πe^- in 

(a) 4 (b) 8
(c) 6 (d) 10

4. Which of the following is least stable?

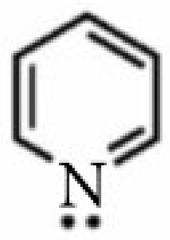
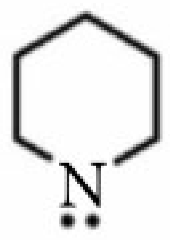
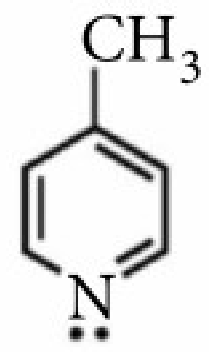
(a)  (b)  (c)  (d) 

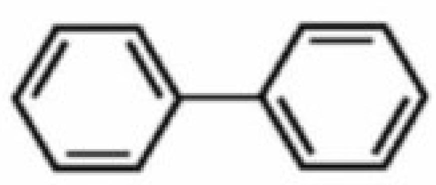
5. Azulene have exceptionally high dipole moment due to

(a) anti-aromaticity
(b) non-aromaticity
(c) aromaticity attained by transfer of e^-
(d) high electronegativity difference.

6. Pyrene + $Br_2 \rightarrow$ Product
If pyrene is aromatic, it undergoes
(a) electrophilic aromatic substitution
(b) elimination
(c) condensation reaction
(d) addition reaction.

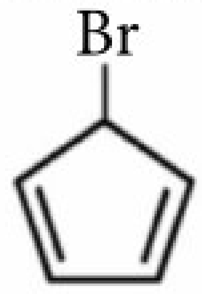
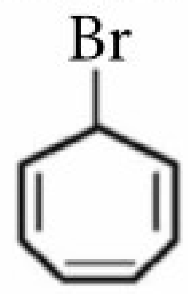
7. Which of the following is least basic?

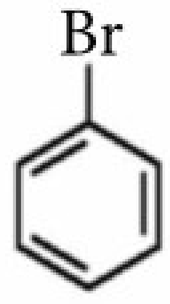
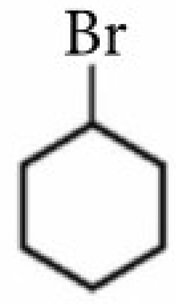
(a)  (b)  (c)  (d) 

8.  is

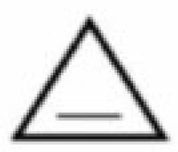
(a) anti-aromatic (b) non-aromatic
(c) aromatic (d) none of these.

9. Which of the following react fast with Ag^+?

(a)  (b) 

(c)  (d) 

10. Which of the following is most acidic ?
(a) *A*
(b) *B*
(c) Both are equally acidic.
(d) None of these is acidic.


(*A*)

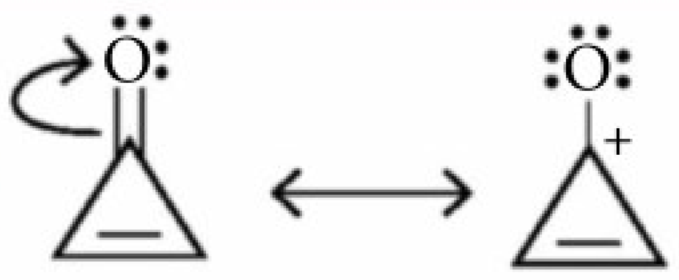

(*B*)

Matching List Type

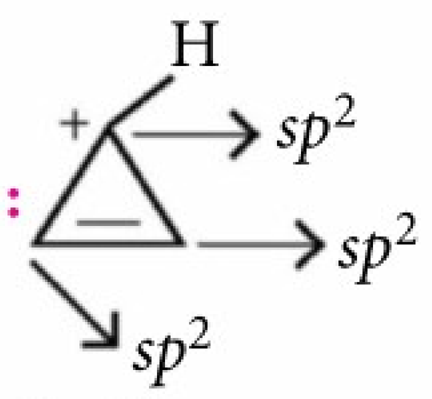
11. Match the following :

(1)	Cyclopentadienyl anion	A.	All 'C' are sp^2 hybridised
(2)	Hexa 1, 3, 5 triene	B.	Compound is anti-aromatic
(3)	Cyclopropene	C.	Complete delocalisation takes place
(4)	Cyclopropenyl anion	D.	Non-aromatic
		E.	Obeys Huckle's rule of aromaticity

Hints & Solutions

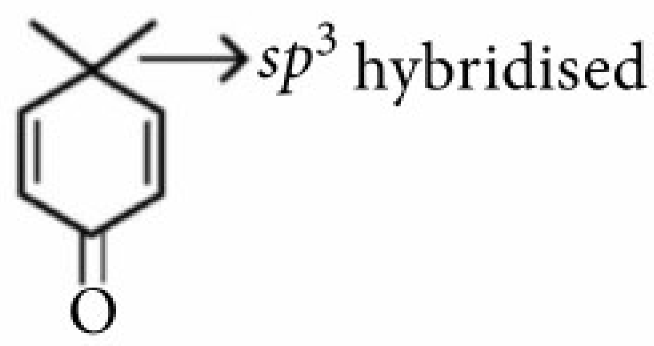
1. **(a) :** 

(i) Cyclic (ii) Planar
(iii) Complete delocalisation
(iv) $(4n + 2)\pi e^- = 2\pi\ e^-$

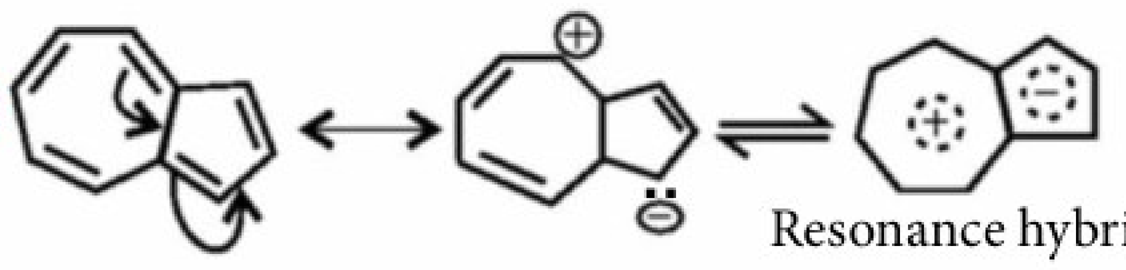
2. **(b) :** 

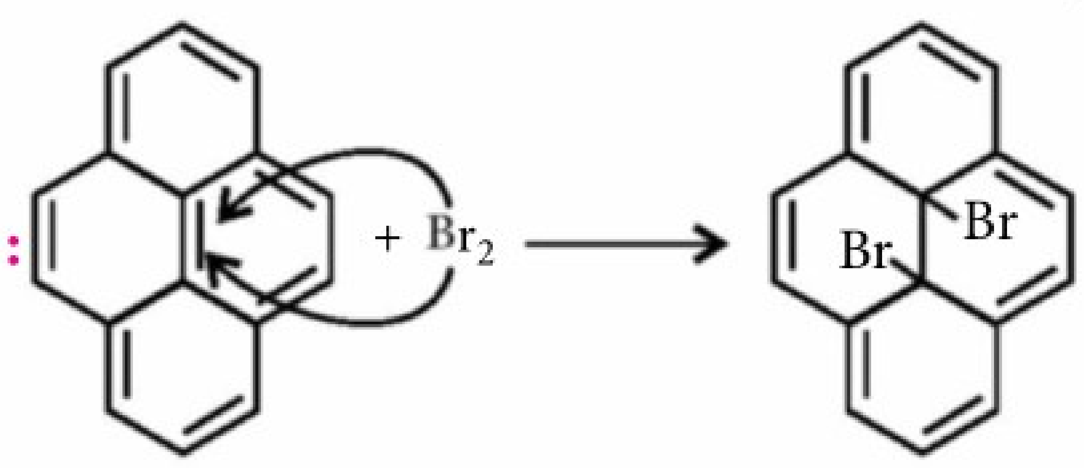
(i) Cyclic (ii) Planar
(iii) Complete conjugation
(iv) $2\pi\ e^-$

3. **(c) :** 2π bonds and 1 *lp* on oxygen involved in delocalisation hence $6\pi\ e^-$

4. **(c) :** It is non-aromatic, 

sp^3 hybridised, non-planar.
Rest of all are aromatic.

5. **(c) :** 
Resonance hybrid

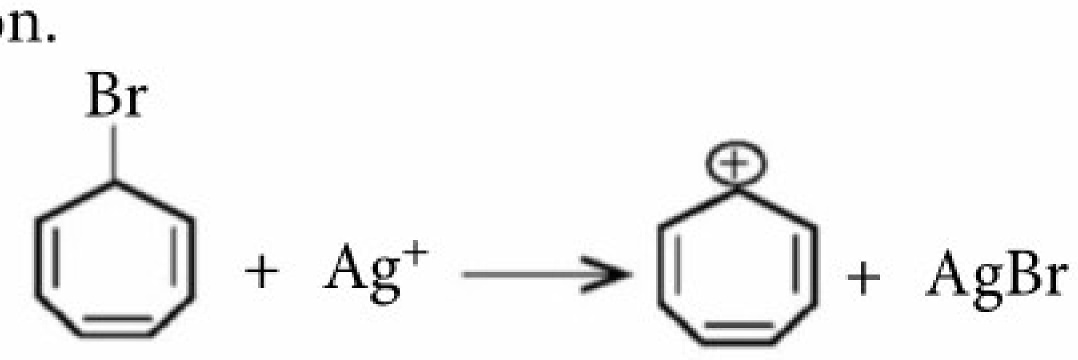
6. **(d) :** 

Central π bond is not involved in delocalisation. It shows addition reaction.

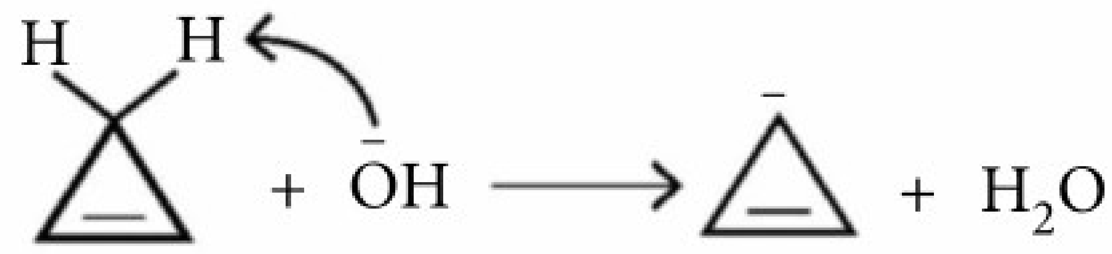
7. **(a) :** Lone pair of 'N' is used for aromaticity which further gives stability. Hence, less available for donation.

8. **(c) :** In biphenyl even though, total number of π electrons are $12(4n\pi)$ it maintains aromaticity in each cyclic ring separately.

9. **(b) :** Because it becomes aromatic by loosing Br^- ion.



Non-aromatic Aromatic

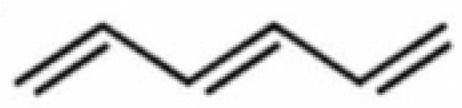
10. **(b) :** 

Non-aromatic (*A*) Anti-aromatic (unstable)

Non-aromatic (*B*) Aromatic (stable)

11. $1 \rightarrow A, C, E$; $2 \rightarrow A, C, D$; $3 \rightarrow D$; $4 \rightarrow A, B, C$

All 'C' sp^2 hybridised, conjugation throughout the ring and $6\pi\ e^-$ available.

(2) 

All 'C' sp^2 hybridised, complete conjugation non-cyclic, hence a non-aromatic.

(3) 

Non-planar, non-conjugation, hence non-aromatic.

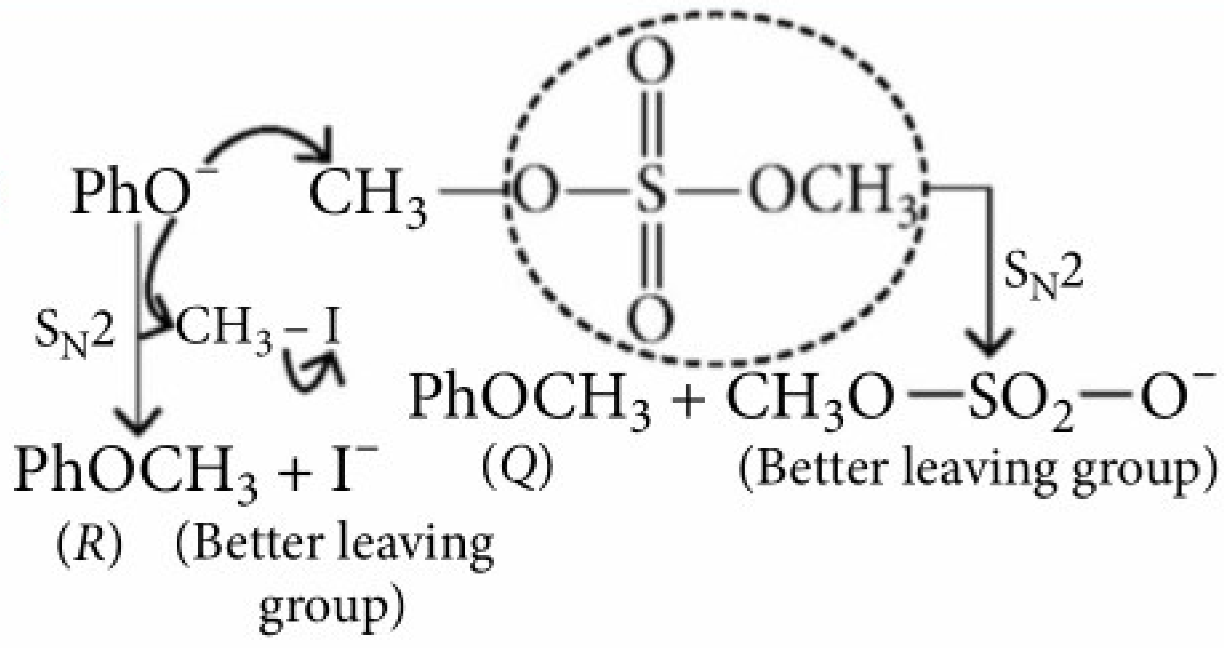
(4) 

All 'C' sp^2 hybridised, $4\pi e^-$ complete conjugation hence anti-aromatic

CHEMISTRY MUSING

SOLUTION SET 74

1. **(a) :**



2. **(b) :** $[Fe(H_2O)_5NO]^{2+}$

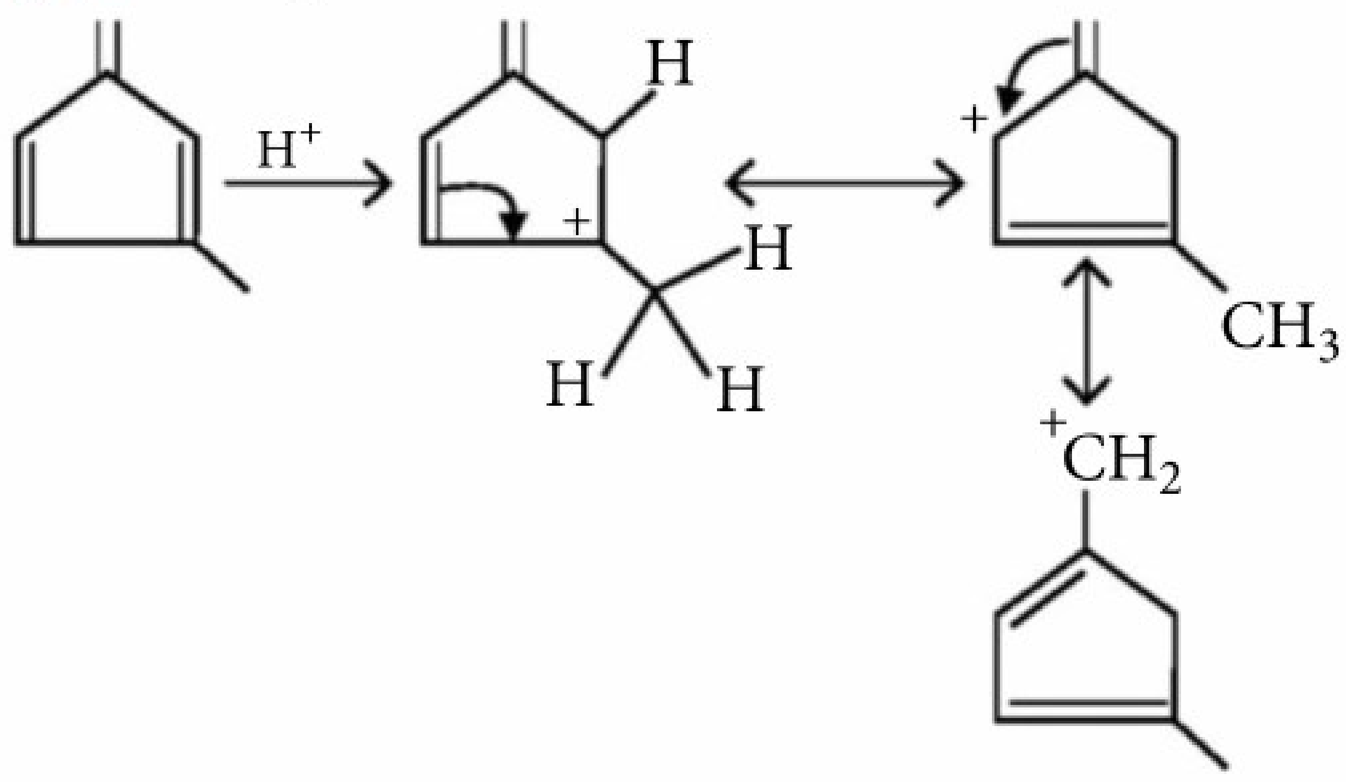
Here, Fe has +1 oxidation state.

Hybridisation: sp^3d^2 ($n = 3$), μ_{eff} : 3.89 B.M.

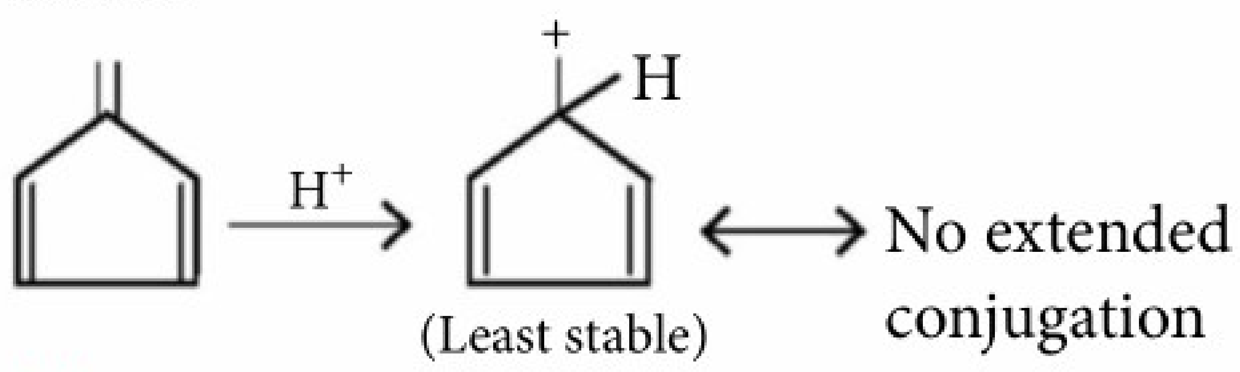
Inspite of electronic transition from NO to Fe^{2+}, total number of electrons remain same.

Hence, EAN does not change.

3. **(a) :** After protonation carbocation is formed.



Extended resonance makes the carbocation more stable.



4. **(a) :** Let the degree of dissociation in both the reactions be α.

	$X \rightleftharpoons$	$2Y$;	$Z \rightleftharpoons$	P +	Q
Initial no. of mol	a	0	b	0	0
At eqm.	$a(1-\alpha)$	$2a\alpha$	$b(1-\alpha)$	$b\alpha$	$b\alpha$

Total no. of moles =

$a(1-\alpha) + 2a\alpha = a(1+\alpha)$; $b(1-\alpha) + b\alpha + b\alpha = b(1+\alpha)$

Mole fractions :

$$X_X = \frac{1-\alpha}{1+\alpha}, X_Y = \frac{2\alpha}{1+\alpha}, X_Z = \frac{1-\alpha}{1+\alpha}, X_P = X_Q = \frac{\alpha}{1+\alpha}$$

Partial pressure :

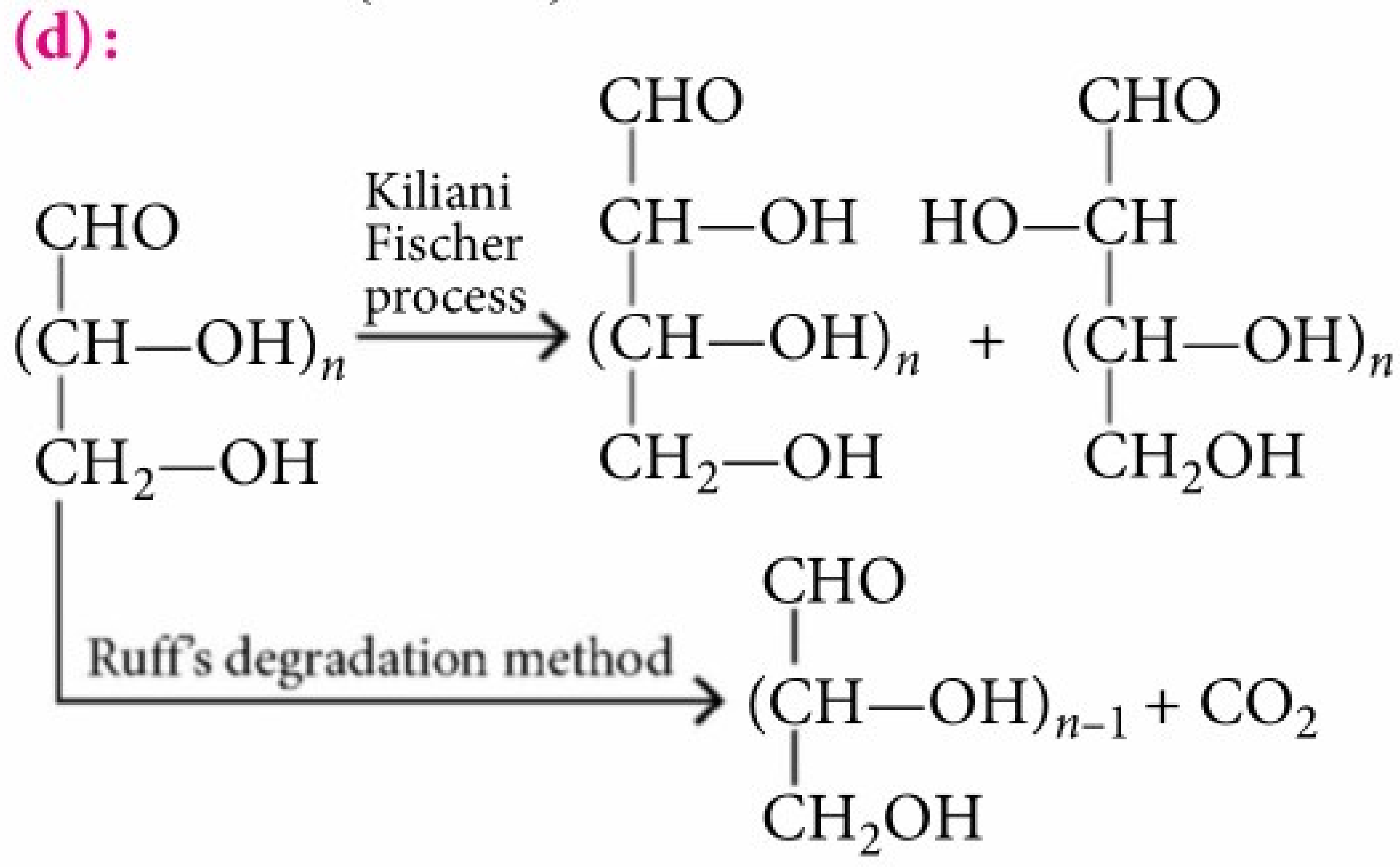
$$p_X = \frac{1-\alpha}{1+\alpha}P_1, p_Y = \frac{2\alpha}{1+\alpha}P_1, p_Z = \frac{1-\alpha}{1+\alpha}P_2, p_P = p_Q = \frac{\alpha}{1+\alpha}P_2$$

Then, $$K_{P_1} = \frac{p_Y^2}{p_X} = \frac{\left(\frac{2\alpha}{1+\alpha}P_1\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P_1\right)} = \frac{4\alpha^2 P_1}{1-\alpha^2},$$

$$K_{P_2} = \frac{p_P p_Q}{p_Z} = \frac{\left(\frac{\alpha}{1+\alpha}P_2\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P_2\right)} = \frac{\alpha^2 P_2}{1-\alpha^2}$$

$$\therefore \frac{K_{P_1}}{K_{P_2}} = \frac{\left(\frac{4\alpha^2 P_1}{1-\alpha^2}\right)}{\left(\frac{\alpha^2 P_2}{1-\alpha^2}\right)} = \frac{4P_1}{P_2} = \frac{1}{9} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

5. **(d) :**



CHEMISTRY PUZZLE SOLUTION SEPTEMBER 2019

BEAKER	BELL JAR
BOILING TUBE	BOTTLE
BUCHNER FLASK	BUCHNER FUNNEL
BURETTE	CONDENSER
CRUCIBLE	DESSICCATOR
ERLENMEYER BULB	ERLENMEYER FLASK
EUDIOMETER	EVAPORATING DISH
FLORENCE FLASK	FREIDRICH CONDENSER
FUNNEL	GRADUATED CYLINDER
JAR	MICROSCOPE SLIDE
PETRI DISH	PIPETTE
RETORT	SEPARATORY FUNNEL
STIRRING ROD	STOPCOCK
TEST TUBE	THISTLE TUBE
VOLUMETRIC FLASK	WATCH GLASS

6. (b) : Packing fraction = $\dfrac{\text{Area occupied by circle}}{\text{Area of unit cell}}$

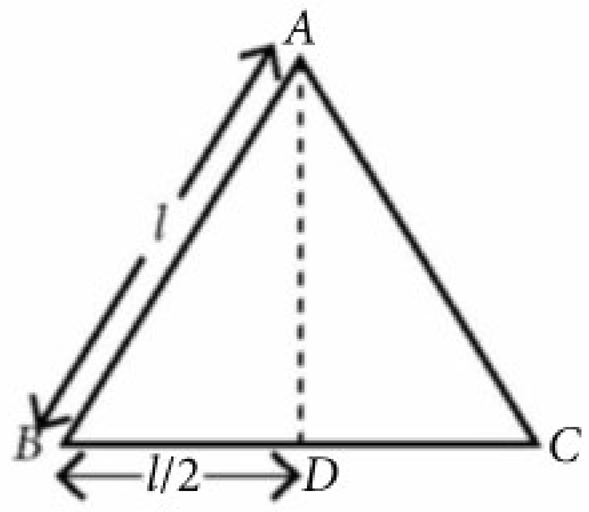
Let edge length = l

Thus, radius (r) = $l/2$

From figure, it is clear that parallelogram has one complete circle. Thus, area of circle = $\pi r^2 = \pi\left(\dfrac{l}{2}\right)^2$

Area of parallelogram = 2 (area of ΔABC)

Area of $\Delta ABC = \dfrac{1}{2} BC \times AD$



$AD^2 = AB^2 - BD^2$

$= l^2 - \dfrac{l^2}{4} = \dfrac{3l^2}{4}$

$\therefore\ AD = \sqrt{3}\left(\dfrac{l}{2}\right)$

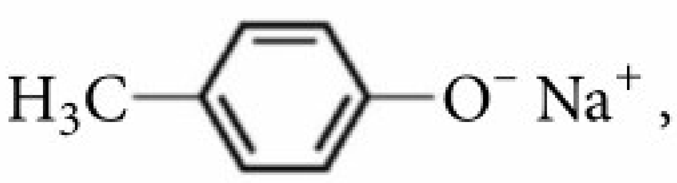
$\therefore$ Area of $\Delta ABC = \dfrac{1}{2}\left(l \times \sqrt{3}\dfrac{l}{2}\right) = \sqrt{3}\dfrac{l^2}{4}$

$\therefore$ Area of parallelogram = 2 × Area of ΔABC

$= 2\sqrt{3}\dfrac{l^2}{4} = \sqrt{3}\dfrac{l^2}{2}$

$\therefore$ Packing fraction = $\dfrac{\pi l^2/4}{\sqrt{3}l^2/2} = \dfrac{\pi}{2\sqrt{3}} = 0.907$

7. (b) : In original mixture only N, N-dimethylaniline forms salt with HCl and that is soluble in NaOH. Amongst remaining, only benzoic acid and p-cresol can form salt with NaOH.



, $C_6H_5COO^-Na^+$

Further only $C_6H_5COO^-Na^+$ can exist in $NaHCO_3$ layer (Test to distinguish phenol and carboxylic acid).

8. (d) : Benzaldehyde forms bisulphite with $NaHSO_3$.

9. (0.4) : CO_2 is reduced to CO when it is passed over red hot coke.

$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$

Since 1 volume of CO_2 produces 2 volume of CO, had all of the CO_2 been converted to CO, the final volume of gas would have been 2 L. However, the final volume is less than 2 L, so some CO_2 must have remained unchanged.

Let x L of CO_2 changed into CO.

Then the volume of the CO_2 left = $(1 - x)$ L

And the volume of CO produced = $2x$ L

The total volume of gas = $(1 - x)$ L + $2x$ L = $(1 + x)$ L

$(1 + x)$ L = 1.6 L

$\therefore\ x = 0.6$

Thus, the composition of the gaseous mixture :

$CO_2 = (1 - 0.6)$ L = 0.4 L , CO = 2 × 0.6 L = 1.2 L

10. (89.24) : $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

	A	B
At $t = 0$	2 mol litre^{-1}	0
At eq.	$(2 - X)$ mol litre^{-1}	X

$k_1 = 2 \times 10^{-3}$ mol L^{-1} s^{-1} (zero order)

$k_2 = 3 \times 10^{-3}$ s^{-1} (1st order)

$$\frac{dX}{dt} = k_1[A]^0 - k_2[B]^1$$

At equilibrium, $\dfrac{dX}{dt} = 0 \quad \therefore\ 0 = k_1 - k_2[X]_{eq.}$

$\therefore\quad [X]_{eq.} = \dfrac{k_1}{k_2} = \dfrac{2\times10^{-3}}{3\times10^{-3}} = 0.66$ mol litre^{-1}

	A $\rightleftharpoons$	B
At initial eq.	1.34	0.66
At eq. Moles added	1.34	0.66 + 0.5 = 1.16
At time t	$(1.34 + X)$	$(1.16 - X)$

Addition of B will bring backward reaction at time t.

$\because\quad [B] = \dfrac{3}{4}[A]_{eq.} = \dfrac{3}{4} \times 1.34 = 1.005$

$(1.16 - X) = 1.005 \quad \therefore\ X = 0.155$

Now, $\dfrac{dX}{dt} = k_1 - k_2[X] = 0.66k_2 - k_2X = k_2(0.66 - X)$

$\therefore\quad \dfrac{dX}{(0.66 - X)} = k_2 \cdot dt$

or $\quad -2.303 \log(0.66 - X) = k_2 \cdot t + C$

At $t = 0$, $X = 0 \quad \therefore\ C = -2.303 \log 0.66$

$\therefore\quad k_2 \cdot t = 2.303 \log \dfrac{0.66}{0.66 - X}$

$$t = \frac{2.303}{3\times10^{-3}} \log \frac{0.66}{0.66 - 0.155} = 89.24\ \text{s}$$

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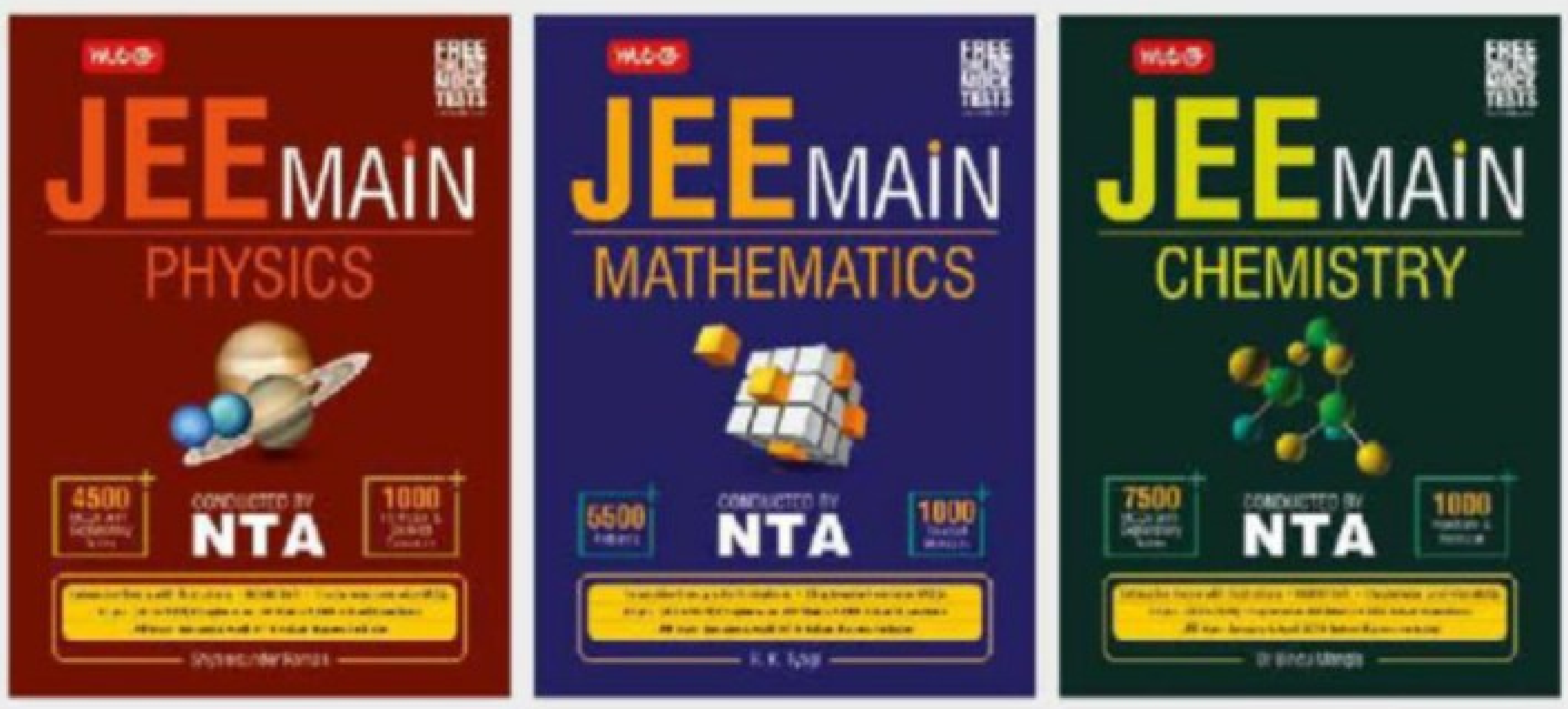

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